

Evaluating the photocatalytic degradation efficacy of 2,4,6-trichlorophenol: performance evaluation and influencing factors

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ABSTRACT

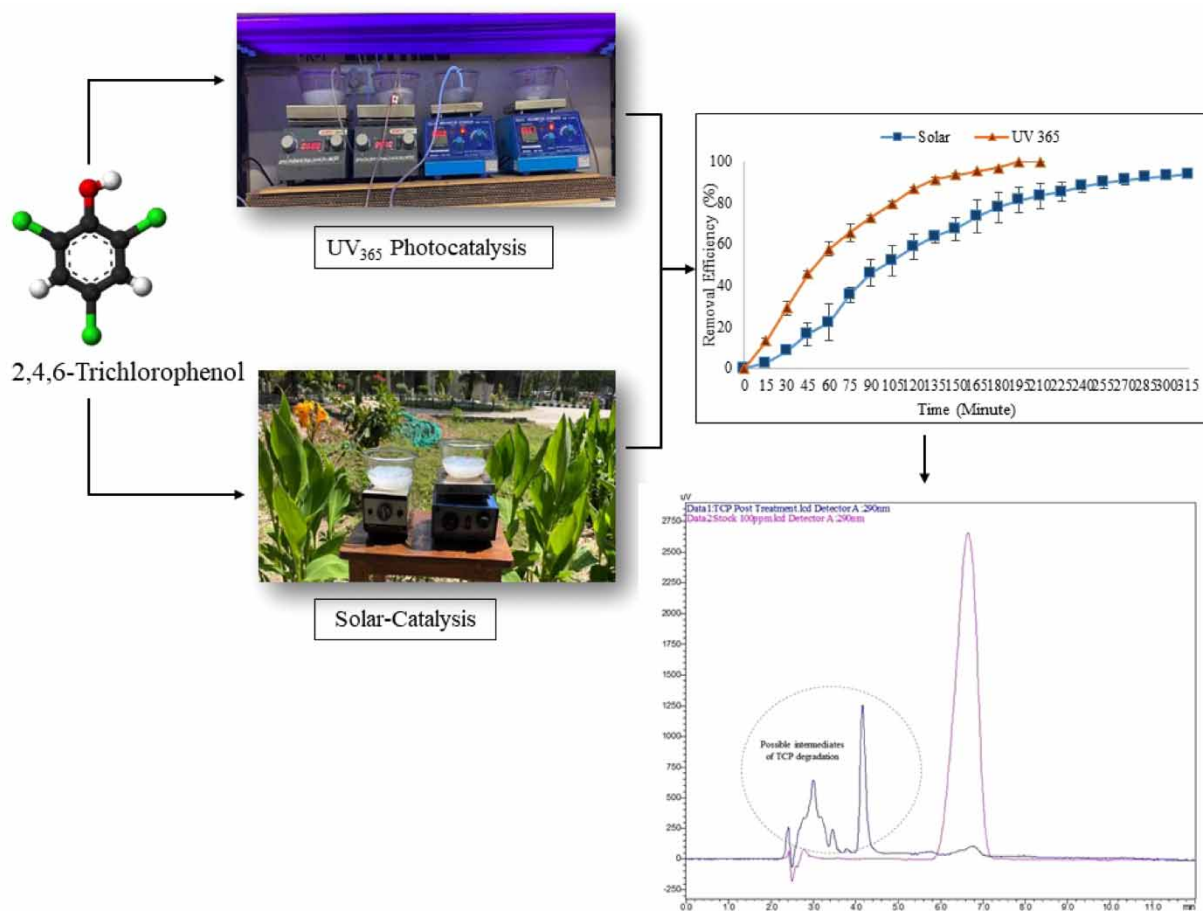
Chlorophenols are organic compounds that have garnered considerable attention in recent years because of their prevalent occurrence in the environment and associated harmful effects on ecosystems and human health. The current work investigated the photocatalytic oxidation of 2,4,6-trichlorophenol as a potential treatment option. The effects of different process-conditioning parameters were studied. Analytical-grade commercially available TiO₂ reported 80% degradation, whereas nano-grade TiO₂ resulted in complete removal in the same time duration. Furthermore, the study assessed the use of Degussa P-25 nano-TiO₂ at varying doses for the optimization of treatment. Under the optimal dose of 250 mg/L of nano-TiO₂, the complete removal of 2,4,6-trichlorophenol was observed within 210 min of the reaction period. The addition of H₂O₂ to further increase the rates of treatment did not yield any benefit. Under solar irradiation, almost 95% degradation of 2,4,6-trichlorophenol was observed in 315 min at an optimized photocatalyst dose. Moreover, the comparison of the operational cost of UV-photocatalysis (UV/nano-TiO₂), photocatalysis with H₂O₂ (UV/nano-TiO₂/H₂O₂) and solar-photocatalysis revealed costs of US\$0.27 per litre, US\$0.30 per litre and US\$0.16 per litre, respectively, during the experimentation, thus making solar-photocatalysis the best option.

Key words: Degussa P-25 nano-TiO₂, H₂O₂, mineralization, photocatalysis, solar-photocatalysis, trichlorophenol

HIGHLIGHTS

- Photochemical oxidation of 2,4,6-trichlorophenol (TCP) using nano-TiO₂ is a potential treatment method.
- The degradation method reported 71% mineralization of TCP based on analysis of total organic carbon.
- High-performance liquid chromatography confirmed 99% degradation of TCP and revealed the formation of a few intermediates during the photocatalytic oxidation.

GRAPHICAL ABSTRACT



ABBREVIATIONS

| | |
|-------|---|
| AOPs | advanced oxidation processes |
| CPs | chlorophenols |
| DCPs | dichlorophenols |
| eV | electron volt |
| HPLC | high-performance liquid chromatography |
| MCPs | monochlorophenols |
| TCP | 2,4,6-trichlorophenol |
| TOC | total organic carbon |
| USEPA | United States Environmental Protection Agency |

1. INTRODUCTION

The continuous release of organic pollutants from industrial units is causing the deterioration of the quality of aquatic ecosystems. The widespread use of chlorinated organics in industrial and manufacturing processes has resulted in the introduction of toxicity in the aquatic environment. The bleaching unit in the textile industry and pulp and paper industry generates effluent loaded with chlorinated aromatic organics (Ahlborg *et al.* 1980). According to a report, the production of one ton of paper requires 100 kg of colour-imparting materials and around 2–5 kg of organochlorides to the bleaching section, resulting in the introduction of chlorophenols (CPs) in the wastewater generated (Nagarathnamma *et al.* 1999). CPs possess broad-spectrum bactericidal properties and, thus, find an application as preservatives in the wood-processing industry, paints, leather, vegetable fibres, and as disinfectants. The compound 2,4,6-trichlorophenol (TCP) is one of the most

commonly formed chlorinated compounds during dechlorination of water. These compounds are widely applied in agricultural fields as herbicides, pesticides and insecticides. Health organizations and environmental pollution agencies have recommended 0.1 and 200 µg/l as the maximum permissible concentrations of CPs in drinking water and wastewater, respectively (ATSDR 1999). Owing to the widespread use of CPs, residues of such compounds are continually detected in soils, sediments, surface water, groundwater and in the trophic levels of food chains. There has been increasing concern for the adverse effects of CPs on environmental damage and human health (Mukherjee *et al.* 2022). CPs are categorized as the priority toxic pollutants listed by the United States Environmental Protection Agency (USEPA) (ATSDR 2007) and can bioaccumulate in organisms (de Souza *et al.* 2021). The toxicity of CPs increases with the increase in the number of chlorine atoms present at ortho- and para- positions, which are more stable than chlorine present at the meta-position. These compounds absorb light with a wavelength of less than 300 nm (a lesser fraction of sunlight), resulting in environmental stability (Bandara *et al.* 2001). At the same time, conventional treatment methods fail to degrade the pollutant as biological treatment is inefficient for decomposition due to the complex structure of the pollutant. On the other hand, advanced oxidation processes (AOPs) have emerged as a promising approach for the treatment of such recalcitrant organic pollutants (Yadav *et al.* 2022). The application of AOPs is reported successful in the treatment of wastewater generated from the pharmaceuticals (Verma & Haritash 2019), textile (Sharma *et al.* 2016; Pipil *et al.* 2022), pesticide, and pulp and paper sector (Cameselle & Gouveia 2018), etc. The processes are governed by the principle of *in situ* generation of highly reactive oxidizing species in the form of hydroxyl radicals (Verma & Haritash 2020). Because of the high reduction potential of OH[•] (2.8 electron volt (eV)), they can oxidize toxicants such as CPs to non-toxic forms such as CO₂ and H₂O. Among AOPs, heterogeneous catalysis has gained popularity because of its inherent destructive potential towards the complete mineralization of organic pollutants. TiO₂ is the most common semiconductor used in the photocatalysis process (Aljuboury *et al.* 2016; Balzani *et al.* 2019). Its high photocatalytic activity, high photochemical reactivity, high stability and lower toxicity towards the environment make it compatible with its use (Thirunavukkarasu *et al.* 2020). When irradiated with a light source, it absorbs photons of energy equivalent to or more than its bandgap width of 3.2 eV. Electrons from the valence band are excited to the conduction band leaving behind holes. Thus, the formation of an electron-hole pair takes place (Equation (1)). Electrons directly react with organic pollutants to form reduction products, whereas holes either react directly with organic compounds or react with water to form hydroxyl radicals which carry out oxidation of harmful organics (Equations (2)–(7)) (Ahmad *et al.* 2016). The following reactions take place during TiO₂-based photocatalysis:



There have been several studies on the removal of polychlorophenols using photocatalysis and Fenton's treatment *in silo* (Pera-Titus *et al.* 2004; Kusvuran *et al.* 2005), but the studies on degradation/mineralization of TCP are very limited. The studies on monochlorophenols and dichlorophenols reported the removal of the contaminants, but limited studies on the degradation of TCPs and its toxicity have been taken into consideration so far. Since the toxicity of CPs is higher as Cl is attached at ortho- and para- positions, the degradation of TCP in textile and pulp and paper industry effluent is pertinent (Yadav *et al.* 2023).

Although the removal efficiency of photocatalytic oxidation is high, the chemical and energy input is also high. To minimize the cost of treatment, optimization of regulating/input parameters should be performed. The present study dealt with the optimization of nano-TiO₂, an option of removing the use of H₂O₂, and the possibility of visible light excitation. In the present study, effort has been made to study the mineralization (degradation) of TCP based on analysis of intermediates of degradation, if any, supported by the analysis of total organic carbon (TOC) before and after photocatalytic oxidation.

Finally, the operational cost of treatment was evaluated for all the options tested for the treatment of TCP-contaminated wastewater.

2. MATERIALS AND METHODS

2.1. Chemicals

The 2,4,6-TCP (purity 98%) was obtained from Thermo Fisher Scientific (USA) and was used for the degradation experiments in the present study. The Degussa P25 nano-TiO₂ (anatase to rutile ratio: 80:20) was obtained from Evonik Industries, Germany; hydrogen peroxide H₂O₂ (30% w/v), which was used as an oxidant, was obtained from Central Drug House (CDH), India; and high-performance liquid chromatography (HPLC)-grade methanol was procured from Merck & Co (India).

2.2. Experimental setup

The photocatalytic degradation of TCP was carried out by varying the dose of TiO₂ and H₂O₂, and optimized conditions were noted. Figure 1 illustrates the treatment system setup of TCP. Keeping the concentration of TCP constant (100 mg/L), varying doses of TiO₂ (50.0–750.0 mg/L) and oxidant (H₂O₂ – 680, 1,700 and 3,400 mg/L) were used to study the removal profile for TCP. The removal study was performed using 200 mL of the synthetic stock solution of TCP of (100 mg/L) in a glass beaker. As the solubility of model pollutant (TCP) is less in water, methanol was used to solubilize the salt, while ultrapure water was later used to top-up the required volume. Prior to photocatalytic degradation, the solution was kept under dark conditions to establish the adsorption/desorption equilibrium of TCP with TiO₂. The aqueous suspension of TCP and photocatalyst was then irradiated under UV light (λ – 365 nm) with continuous stirring and air sparging. The experiments were carried out in a fabricated UV chamber with eight UV tubes (Phillips 36 W each) of wavelength 365 nm. The cumulative source intensity of the UV chamber as calculated by Verma & Haritash (2019) was 672 W/m² with an accumulated energy of 535.1 kJ/L. A sample volume of 5 mL was extracted for analysis using a pre-rinsed syringe at regular intervals of 15 min and was then

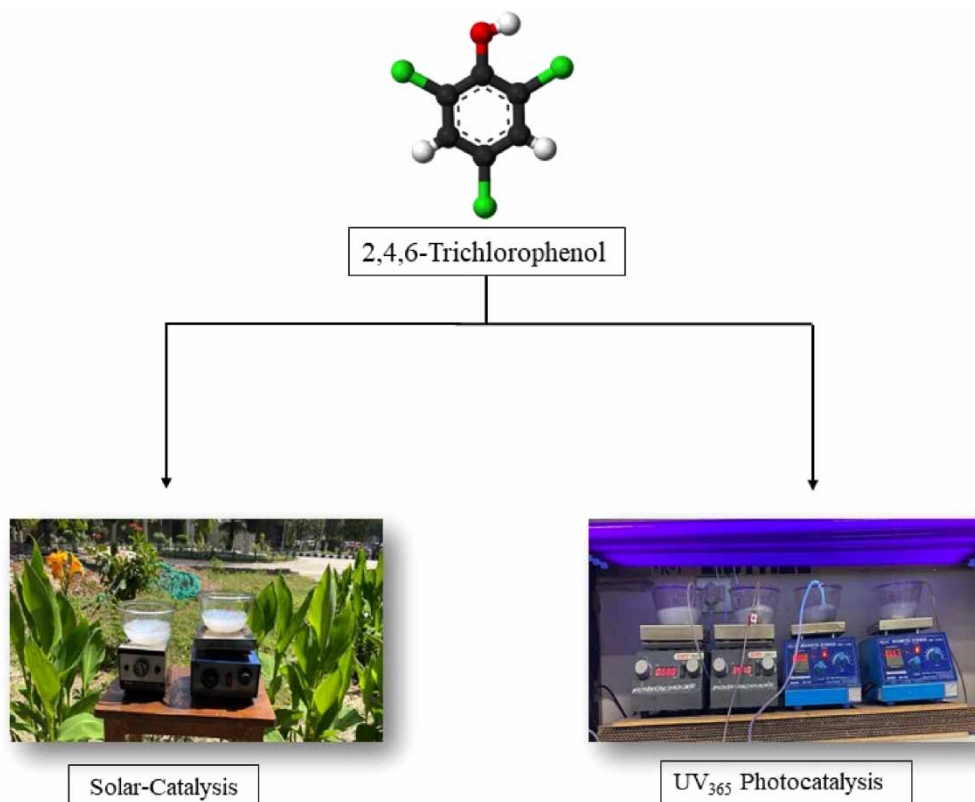


Figure 1 | Treatment system setup of TCP.

subjected to centrifugation at 5,000 rpm for 5 min. The above procedure was repeated until the residual concentration of TCP became constant. All the experiments were carried out in triplicates to ensure the accuracy of the analysis.

2.3. Analysis of 2,4,6-TCP

For continuous detection of the degradation of TCP, a double-beam UV-Vis spectrophotometer (Lab India make UV 3092 model) was used. An absorption spectrum of 2,4,6-TCP was plotted in the wavelength range of 190–800 nm and the wavelength of maximum absorption (λ_{max}) was obtained at 290 nm. The calibration graph for TCP was plotted in the concentration range of 10–100 mg/L at 10 mg/L intervals. The removal efficiency of TCP was calculated using the following equation (Equation (8)):

$$\text{Efficiency (\%)} = \left[\frac{C_i - C_t}{C_i} \right] \times 100 \quad (8)$$

where C_i is the initial concentration of TCP and C_t is the concentration of TCP at time t .

In addition to this, the residual concentration of TCP was confirmed over HPLC (Shimadzu, Japan). The chromatographic investigation was also used to determine the residual reaction intermediates during the photocatalytic oxidation of TCP. The HPLC system (Shimadzu, LC-20AD) equipped with an UV/VIS detector (SPD-20A) and C-18 column (Inertsil[®] ODS-3 V, 5 μm , 4.6 \times 250 mm) was used for the analysis. A standard curve of the model compound (TCP) was plotted in the concentration range of 0–100 mg/L at intervals of 10 mg/L in the HPLC system. Methanol and water (70:30 v/v) were used as a mobile phase at a flow rate of 1.5 mL/min for separation by HPLC, and the response was recorded at 290 nm. Mineralization of TCP was also analysed over a TOC Analyser (TOC-L Shimadzu Make, Japan) to confirm the observation of the UV-Vis spectrophotometer and HPLC.

3. RESULTS AND DISCUSSION

Photocatalytic oxidation of TCP using TiO_2 as a catalyst was found efficient in the removal of the aforementioned pollutant. The study undertook the effect of regulating parameters such as catalyst dose, catalyst size, source of light and the presence of oxidizing agent on the removal efficiency of TCP. The pH of the TCP solution was kept neutral since earlier studies have reported optimum degradation of organic impurities using Degussa P-25 TiO_2 at pH 6.8 (Aljuboury *et al.* 2016).

3.1. Effect of catalyst type

Commercially available analytical grade TiO_2 was analysed against nano- TiO_2 (Degussa P-25) for the degradation of TCP. It was observed that nano- TiO_2 exhibited greater potential towards the removal of TCP. Nano- TiO_2 reported nearly complete degradation (~97%) of TCP within 210 min (3.5 h), whereas analytical grade TiO_2 was able to degrade only 75% of model pollutant during the same irradiation time (Figure 2). The effectiveness of nano- TiO_2 is attributed to the increased surface area and absorption of energy as well as increased internal recombination of electrons and holes and surface active sites (Chen *et al.* 2020).

It could also be observed that in the absence of photocatalyst, UV_{365} alone removed a significant proportion of TCP (~30%), indicating that photolysis also plays a role in the removal of TCP. Considering the edge of nano- TiO_2 over analytical-grade TiO_2 , further experimentation was conducted using nano- TiO_2 for the degradation of TCP.

3.2. Effect of catalyst dose and H_2O_2

The photocatalytic oxidation of TCP (100 mg/L) with different doses of nano- TiO_2 was varied substantially (Figure 3). It can be observed from Figure 3 that the removal rate increased upon increasing the dose of the photocatalyst. At a concentration of 250 mg/L of TiO_2 , complete degradation was achieved after 210 min of irradiation. However, when TiO_2 concentration was increased beyond 250 mg/L, i.e., 275, 300, 500 and 750 mg/L, the degradation rate decreased (Figure 3).

This can be rationalized concerning the availability of active sites on the surface of TiO_2 and the effective penetration of photoactivating light in TCP- TiO_2 suspension. At higher doses of TiO_2 , a turbid suspension inhibits the effective penetration of light. Furthermore, a lesser number of photons is absorbed causing fewer generations of hydroxyl radicals to oxidize TCP, thereby affecting the degradation efficiency, as observed in other studies as well (Verma & Haritash 2020; Pipil *et al.* 2022). The higher degradation efficiency while increasing the dose of TiO_2 is because of the electron-hole pairs generated. The Degussa P-25 nano- TiO_2 consists of rutile and anatase phases (anatase to rutile ratio: 80:20). Anatase TiO_2 exhibits a

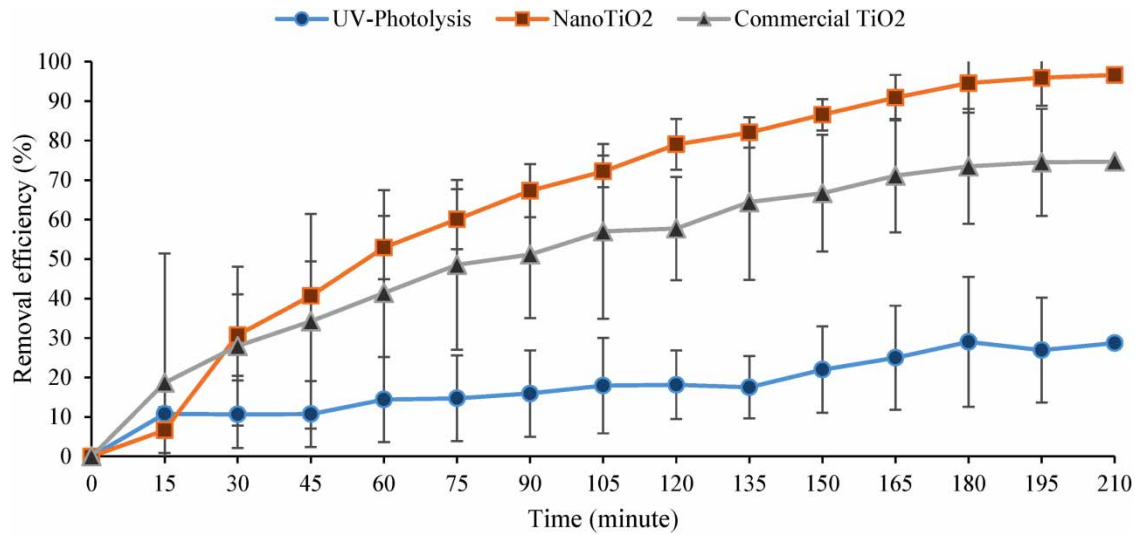


Figure 2 | UV₃₆₅-induced degradation of 2,4,6-TCP using commercial-TiO₂ and nano-TiO₂.

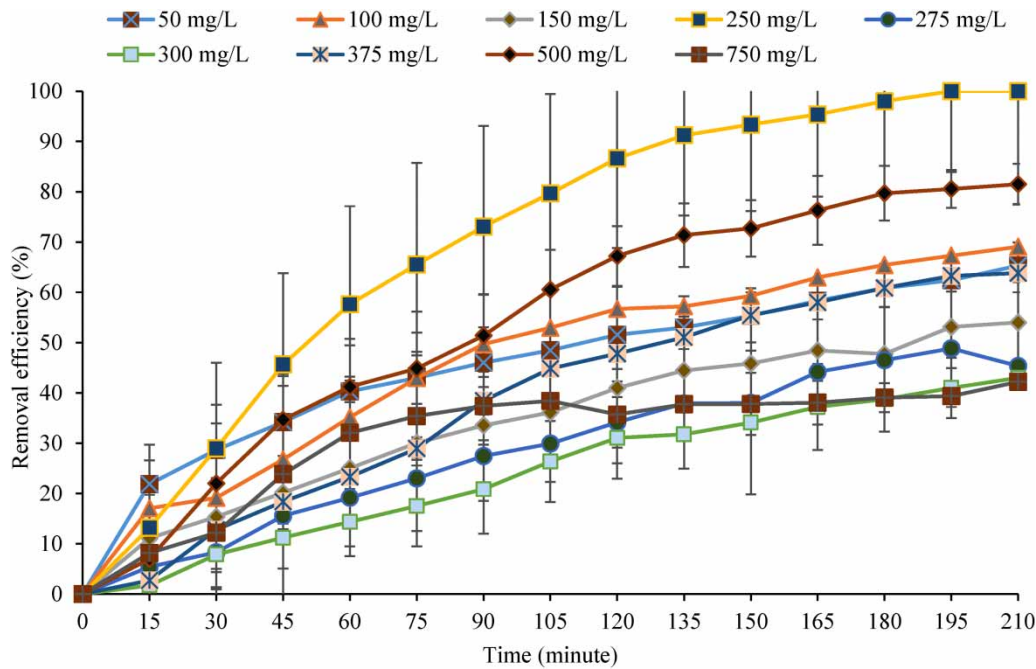


Figure 3 | Removal efficiency of 2,4,6-TCP ($C_i = 100$ mg/L) at varying catalyst doses.

longer period of electron holes with lower recombination of charge carriers. This causes mass migration of electrons and holes from the interior to the surface of anatase TiO₂, whereas the rutile TiO₂ part has a smaller band gap that generates electron-hole pairs when irradiated with low-energy photons, making it advantageous for anatase TiO₂ to utilize these electron-hole pairs (Bagbi *et al.* 2017). Thus, the synergetic effect of rutile and anatase phases of TiO₂ plays a crucial role in photocatalytic efficiency. The generated electron-hole pairs react either directly with the organic pollutant or with surface-bound water to produce hydroxyl radicals. Increasing the amount of TiO₂ increases the availability of active sites, thus increasing the adsorption process too. Hence, the more the binding of electron-hole pairs with water, the more the production of the hydroxyl radicals.

Earlier studies on photocatalytic degradation of TCP revealed that the time for the complete removal of TCP remains extended if optimization for TiO_2 dose is not taken into account. The degradation of TCP ($C_i = 50 \text{ mg/L}$) at a TiO_2 dose of 500 mg/L reported 100% degradation in 240 min (Shoneye & Tang 2020), whereas the present study reports 100% degradation within 210 min for an initial concentration of 100 mg/L TCP but at an optimized TiO_2 dose of 250 mg/L . It may be important to note that optimization resulted in the degradation of two-fold concentrated wastewater with half the amount of TiO_2 in a relatively short time. This may favour the treatment of more volume/concentration of effluent efficiently with reduced cost of treatment based on the results of the present study. It is also important to mention that reaction conditions should be optimized to achieve enhanced treatment efficiency. Some studies report lower reaction times (Rengaraj & Li 2006; Choi *et al.* 2019) compared with this study, but it is because the initial concentration of TCP there was significantly less ($20\text{--}50 \text{ mg/L}$) than the one used (100 mg/L) in the present study. The other reason in a few studies is relatively higher doses of TiO_2 being used for photocatalysis (Pandiyan *et al.* 2002; Choi *et al.* 2019), which adds to the cost of treatment.

H_2O_2 is a strong oxidizing agent, which was added in the experiment to increase the generation of OH radicals and to further enhance the rate of degradation. The effect of the addition of H_2O_2 was studied by varying the concentration at 20, 50 and 100 mM at the optimized dose of TiO_2 (250 mg/L) for the removal of TCP. However, the addition of H_2O_2 did not result in any significant improvement for the removal of TCP in the present study. The efficacy of photocatalytic degradation in the presence of H_2O_2 was reported as less than 80% in 3.5 h among all the above-mentioned experimental setups.

3.3. Solar-induced photocatalysis

Solar energy consumption is almost four orders of magnitude less than the total solar energy irradiating the surface of the Earth (Balzani *et al.* 2019). As no alteration can take place in the solar spectrum, solar energy could be exploited and harnessed to increase the efficiency of the treatment system. Although the proportion of UV light is 3%–5% in natural sunlight, the degradation profile of TCP under natural sunlight (solar-catalysis) using nano- TiO_2 at a concentration of 250 mg/L was also investigated. It was observed that 95% degradation efficiency was attained in 300 min (5.0 h) of sunlight exposure (Figure 4).

It was also noted that with the increase in the solar intensity, the rate of degradation also increased. The average solar influx radiation intensity was 655.5 W/m^2 with accumulated energy of 522.2 kJ/L . Figure 5 represents the degradation profile of TCP as a function of accumulated energy for every 15 min. It has been reported that the rate of electron excitation from the valence band to the conduction band is influenced by the intensity of light affecting the rate of photocatalytic reaction and photocatalyst activation. Thus, higher intensity is directly proportional to photocatalytic oxidation (Yadav *et al.* 2023).

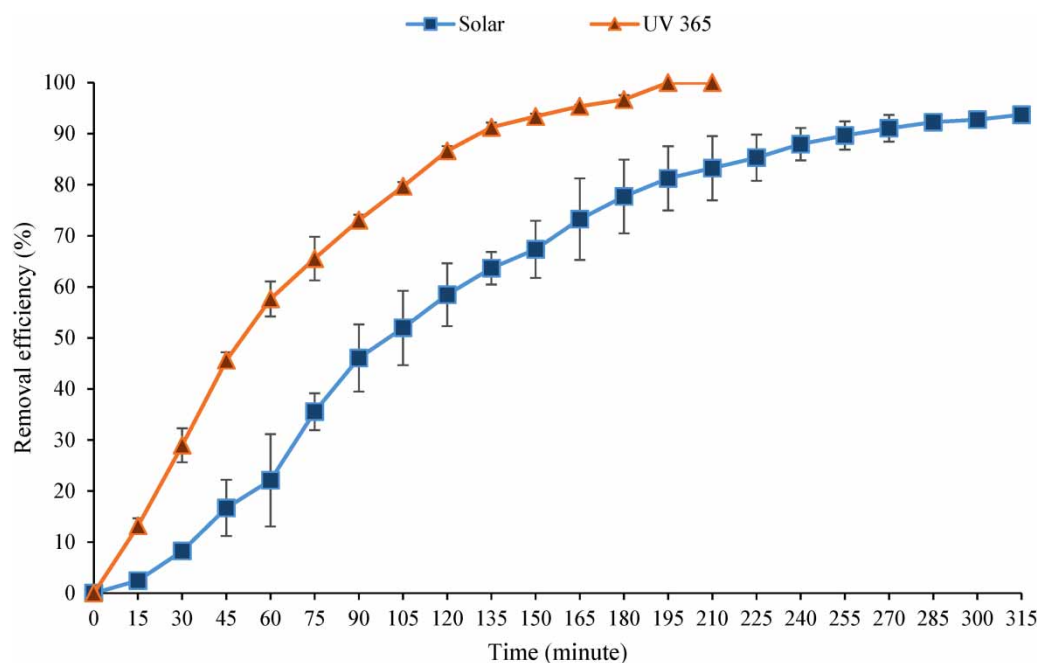


Figure 4 | Removal efficiency of TCP under solar and UV light as a function of time.

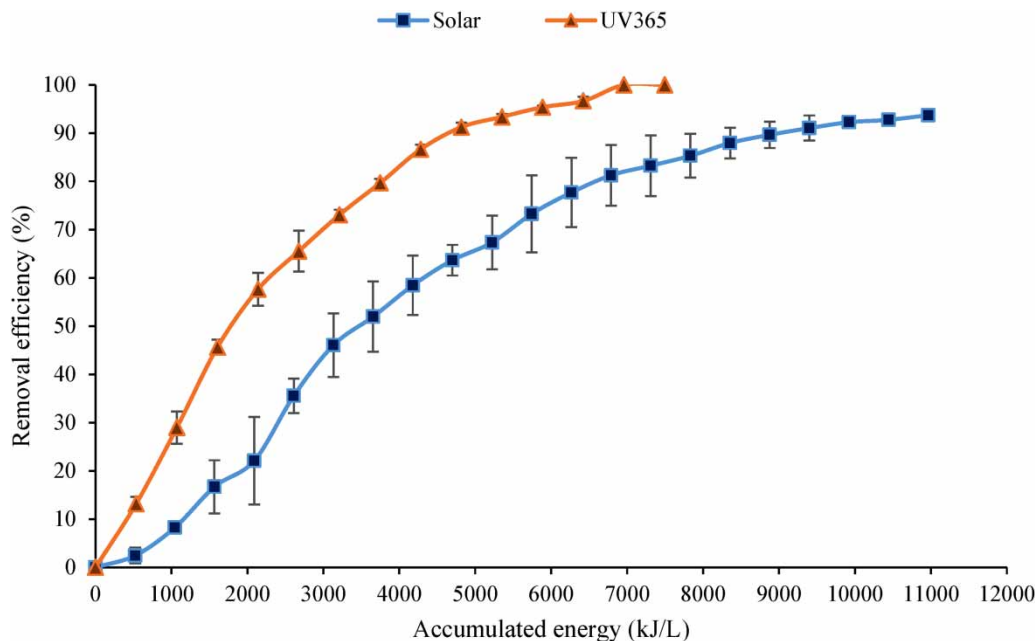


Figure 5 | Removal efficiency of TCP under solar and UV light as a function of accumulated energy.

However, the rate of photocatalysis is no longer affected by the intensity of light beyond the optimum level because of the limited availability of active sites on the surface of the photocatalyst (Blake *et al.* 1991). Based on the results of the present study, it is seen that photo-exposure and catalyst (based on size) can significantly regulate the removal efficiency of TCP during photocatalysis.

3.4. Mineralization of TCP

The degradation of TCP was studied using a spectrophotometer in terms of absorbance of residual concentration at regular intervals. To further confirm the mineralization of the organic compound, TOC analysis was done. The degradation profile revealed that approximately 71% of TCP was mineralized based on analysis of TOC. To monitor the feasibility of the formation of any intermediates, HPLC analysis of TCP pretreated and post-treated samples was done. The analysis over HPLC (Rt: 6.8 min) confirmed 99% degradation of TCP, but it reported the formation of a few intermediates during the photocatalytic oxidation, thus confirming that there are about 29% TOC leftovers in the form of intermediates (Figure 6).

3.5. Economic analysis and recovery of TiO₂

TiO₂ was added as a catalyst in the experiment and was not consumed in the reaction; however, some fraction of TiO₂ was lost during analysis, sample centrifugation, sample transfer, etc. At the end of the reaction process, the leftover TiO₂ was recovered and oven-dried at 105°C. The recovery of TiO₂ was calculated using the following formula:

$$\text{TiO}_2 \text{ recovered} = \frac{w_2}{w_1} \times 100 \quad (9)$$

where w_1 is the initial known weight of TiO₂ added and w_2 is the residual weight of recovered TiO₂. In the present study, ~80% of the TiO₂ added in the experiment was recovered under optimized conditions. Thus, the use of optimized TiO₂ reduces the overall cost of the treatment, making the process environmentally and energy-efficient. The economic analysis was conducted after maximal degradation of TCP, with respect to photocatalysis, solar-photocatalysis and photocatalysis with H₂O₂, and a comparative analysis of operational cost was done (Table 1).

Photocatalysis was carried out in a fabricated UV chamber having eight UV tubes, each having a power rating of 36 W making together 288 W; also the power ratings of the magnetic stirrer and air sparger are 8.5 and 3.5 W, respectively. Therefore, the overall power consumption is 300 W or 0.3 kWh. In the case of solar-photocatalysis, only magnetic stirrer and air

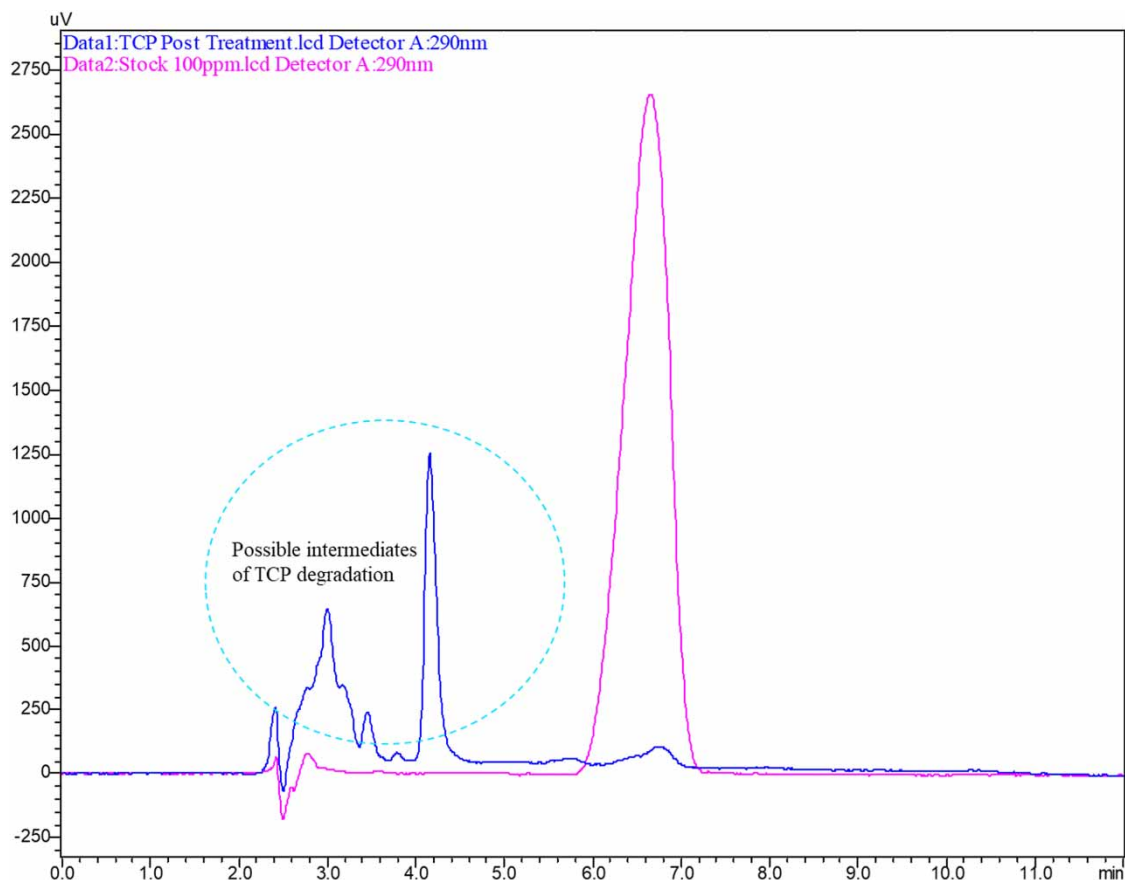


Figure 6 | Chromatogram of TCP before and after degradation depicting the intermediate formation.

Table 1 | Economic analysis of the operating cost of UV₃₆₅ photocatalysis, solar-photocatalysis and UV-photocatalysis with H₂O₂ (with 80% TiO₂ recovery)

| Treatment method | Energy per hour (kWh) | Time for treatment (min) | Rate of energy (per kWh) (INR) | Cost of electricity (INR) | Chemical consumed | Cost of chemical per litre (INR) | Cost of treatment per litre (USD) |
|--|-----------------------|--------------------------|--------------------------------|---------------------------|--|----------------------------------|-----------------------------------|
| UV ₃₆₅ photocatalysis | 0.3 | 210 | 8.50 | 8.9 | Nano-TiO ₂ | 11.34 | 0.27 |
| Solar-photocatalysis | 0.012 | 300 | 8.5 | 0.51 | Nano-TiO ₂ | 11.34 | 0.16 |
| UV-photocatalysis with H ₂ O ₂ | 0.3 | 210 | 8.5 | 8.9 | Nano-TiO ₂ H ₂ O ₂ (30% w/v) | 13.62 | 0.30 |

sparger were used, thus making a power consumption of 12 W or 0.012 kWh. The electricity cost for industrial supply in most of the states in India is INR 8.5 per unit kWh. The complete degradation efficiency of TCP under the UV/TiO₂ system was observed in 210 min with a photocatalyst dose of 250 mg/L. The cost of nano-size TiO₂ (P25) is INR 22,680 per 100 g but only 20% of it was consumed while 80% was recovered. Therefore, the cost of the photocatalyst is INR 11.34 per litre for synthetic wastewater treatment (for 250 mg/L dose of TiO₂) in UV/TiO₂, UV/H₂O₂/TiO₂ and solar/TiO₂ systems. Thus, the overall operational cost of the UV/TiO₂ treatment process is INR 14.57 or US\$0.27. In the case of UV/H₂O₂/TiO₂, the additional cost of oxidant chemicals occurred, making together the cost of treatment per litre US\$0.30. However, a considerable cost of treatment was saved in the case of solar-photocatalysis (US\$0.16 per litre).

4. CONCLUSION

CPs give rise to significant environmental concerns owing to their toxicity, carcinogenicity and bioaccumulation potential, especially in the aquatic environment. Inefficient treatment of these xenobiotics in industrial effluents and discharge of partially treated wastewater further aggravate the environmental and health issues. The present study reported the efficacy of photocatalytic oxidation as a potential method for the removal/degradation of 2,4,6-TCP. The removal efficiency of the treatment methods follows the order of $80\% < 95\% < 100\%$ for UV/nano-TiO₂/H₂O₂ < solar-photocatalysis < UV-photocatalysis, respectively. The rate of reaction was faster in the case of UV-photocatalysis; however, it may be replaced by solar for low-strength or low-volume wastewater, further reducing the burden of cost. Despite the non-avoidable cost associated with chemicals and energy input, optimization of such chemical oxidation methods can significantly reduce the operational cost as observed in the case of catalyst optimization. Compared with the limited removal rate of conventional treatment and persistence of CPs in the environment, photochemical oxidation using nano-TiO₂ is a promising treatment approach, since it leads to the mineralization of TCP and elimination of associated residual toxicity besides bringing down the organic load in wastewater. Additionally, the cost of treatment of effluent is a governing factor for industries and solar-induced removal of such contaminants could be a cost-effective approach. As no modification in the solar spectrum can take place, solar energy could be exploited and harnessed to increase the efficiency of the treatment system. Thus, solar-photocatalytic oxidation can serve as a sustainable treatment option for the degradation of 2,4,6-TCP considering its benefits to the environment and health.

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AUTHORS' CONTRIBUTIONS

H. Pipil and S. Yadav contributed to the conceptualization, execution, data compilation and draft writing of this research. S. Kumar and A. K. Haritash contributed to the conceptualization as well as supervising, reviewing and editing the manuscript.

DATA AVAILABILITY STATEMENT

All relevant data are included in the paper or its Supplementary Information.

CONFLICT OF INTEREST

The authors declare there is no conflict.

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