

Photocatalytic oxidation of 2,4,6-trichlorophenol in water using a cocurrent downflow contactor reactor (CDCR)

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Abstract

The heterogeneous photocatalytic oxidation of aqueous solutions of 2,4,6-trichlorophenol (2,4,6-TCP) as a model pollutant in industrial wastewater has been carried out in a pilot scale cocurrent downflow contactor reactor (CDCR). The reactions were carried out in the presence of Ultra-Violet radiation, O₂ and TiO₂ photocatalyst (VP Aeroperl P25/20). The TiO₂ was characterized by Dynamic Vapour Sorption (DVS) technique giving specific surface area and surface energy of 46.06 m² g⁻¹ and 80.12 mJ m⁻², respectively. The CDC reactor was fitted with an internally and vertically mounted 1.0 kW or 2.0 kW UV lamp. The reactions were carried out at 50 °C and 1 bar, with the reactor being operated in closed loop recycle mode and suspended photocatalyst being re-circulated. The CDC reactor, a device of very high mass transfer efficiency giving unusually large gas hold-up of approximately 50%, was operated with oxygen mass transfer and dissolution in the zone above the UV lamp (high mass transfer zone) and along and around the UV lamp housing (reaction zone).

Under optimized reaction conditions, 100% conversion of 2,4,6-TCP was achieved in 180 min using 15 dm³ solutions with initial concentration of 120 mg dm⁻³. A combination of TiO₂ photocatalyst, UV irradiation and oxidant was observed to give the most rapid photodegradation and photomineralization of the 2,4,6-TCP in comparison with irradiation only. Using the 1 kW or 2 kW UV lamps, conversion of 100 mg dm⁻³ of 2,4,6-TCP after 30 min was 62.51% and 90.71%, respectively, with initial reaction rates of 1.33 × 10⁻⁵ and 4.22 × 10⁻⁵ mol min⁻¹, respectively, and rate constants 0.0046 and 0.29 min⁻¹, respectively.

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1. Introduction

In a world faced with ever increasing population and ever tightening regulations in the treatment of aqueous and gaseous wastes, the need for efficient treatment of industrial wastewaters and contaminated drinking water sources has led to the research and development of novel treatment methods. Photocatalytic oxidation, an advanced oxidation process (AOP), is one of the relatively new novel treatment processes. An ideal waste treatment technology will achieve complete mineralization of all toxic substances present in the waste stream and should be cost-effective [1]. These technologies are not only required to decompose toxic industrial wastewater effluents and contaminants in drinking water sources, but

are also required to improve the quality of water. One such technology that can efficiently degrade and mineralize toxic pollutants in industrial wastewaters and contaminated drinking water is the cocurrent downflow contactor reactor (CDCR) [2–4].

The CDCR is a mass transfer efficient gas–liquid contactor, where the gas and liquid phases are introduced downwards and cocurrently through an orifice and entry zone at the top of a fully flooded column. The column consists of two sections, the upper section (high mass transfer zone) and the bottom section (irradiation zone). In the upper section of the column, a vigorously agitated gas–liquid dispersion is created by the high velocity liquid jet inlet stream. The dispersion consists of nearly uniformly sized bubbles of 4–5 mm for O₂/H₂O system and these bubbles are in a closely packed array. The turbulence, mixing and high shear created in this upper section of the column causes an efficient gas–liquid contacting and very high mass transfer of oxygen into the liquid phase.

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Advantages of the CDCR over conventional reactor configurations are [2]:

- lower power consumption,
- 100% gas utilization and 97% approach to equilibrium in short times,
- easy scale-up without any loss in mass transfer efficiency,
- control of bubble interfacial area ($1000\text{--}6000\text{ m}^2\text{ m}^{-3}$) depending on bubble size,
- high gas hold up (0.5–0.6),
- tolerance to particles and therefore suitable for slurry chemical reaction,
- conventional and structured catalysts can be used.

Typical values of $k_L a$ (the volumetric gas–liquid mass transfer coefficient) for $\text{O}_2/\text{H}_2\text{O}$ systems are in the range $0.25\text{--}1.5\text{ s}^{-1}$ and are found to be greater than $k_L a$ values for more conventional bubble column reactors for the same reaction [3,4].

The use of advanced oxidation processes (AOPs) such as photocatalytic oxidation, for water and wastewater treatment has been an interesting and attractive subject of research for the past 15–20 years, with various model pollutants studied using various reactor configurations [1,4–14]. The governing principle of AOPs is the formation of hydroxyl radicals which are considered to be the principal oxidizing agent for organic pollutants, with an exceptionally high oxidation potential (2.8 eV) compared to other oxidizing species [4]. These hydroxyl radicals attack organic pollutants in water to convert them to CO_2 and H_2O and mineral acids (for N, Cl and S containing compounds). A summary of compounds degraded by various researchers using photocatalysis including information about the UV source used, photocatalyst used and intermediates detected has been reported by Bhatkhande et al. [15]. The principles governing the photocatalytic oxidation of organic species on a semiconductor material (TiO_2), and a reaction scheme can be found in Winterbottom et al. [4]. The Mechanism of photocatalytic oxidation of organic pollutants and the kinetics of degradation and mineralization have been published by several authors [6,11,13,14,16–32].

Chlorophenols are among most widely spread toxic pollutants in water and wastewater and they belong to a notable group of pollutants called priority pollutants because they are highly toxic and are also known to be potential carcinogens and mutagens. They are therefore listed among the U.S. Environmental Protection Agency and the European Community red list of priority pollutants [11,33]. The presence of chlorophenols in industrial waste streams and water sources has recently become a great environmental concern. The most recent legislation in the European Union in this regard was the European Water Framework Directive WFD, Directive 2000/60/EC.

A general reaction scheme for the heterogeneous photocatalytic oxidation of chlorophenols is



The primary objectives of this study were to investigate the behaviour of the cocurrent downflow contactor reactor (CDCR) for the heterogeneous photocatalytic degradation and mineralization of 2,4,6-TCP as a typical model pollutant and also

demonstrate the applicability of the CDCR for scale-up for industrial scale treatment of effluents. Several different techniques can be employed to generate hydroxyl radicals with all methods involving the use of an oxidizing agent (H_2O_2 , O_3 , O_2) together with an activating system (UV light or photocatalyst). Some of the variables and techniques that influence the photocatalysis process have been investigated and these variables and the CDCR operating conditions were optimized to achieve 100% degradation and mineralization of the 2,4,6-TCP. These variables include operating conditions of the CDCR, photocatalyst loading, operating temperature, oxygen flow rate, UV lamp power and reaction systems (different UV processes).

2. Experimental

2.1. Photocatalytic reactor (the CDCR)

All reactions were carried out using the cocurrent downflow contactor reactor (CDCR) constructed from standard QVF glass fittings. A schematic representation of the photocatalytic CDCR is shown in Fig. 1. Gas and liquid streams are introduced concurrently through an orifice in the entry zone at the top of a fully flooded column. The reactor comprises two independent

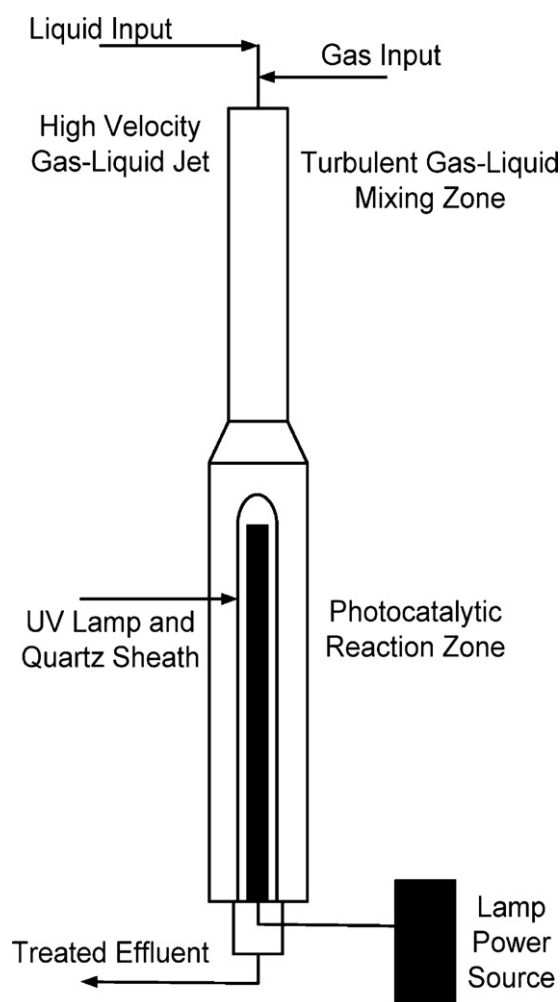


Fig. 1. Schematic diagram of the CDCR.

Table 1
CDC photocatalytic reactor (CDCR) operating conditions

| Parameter | Reactor |
|---|-----------|
| Reaction zone volume (dm ³) | 4.0 |
| Orifice diameter (m) | 0.005 |
| Recirculation rate (dm ³ min ⁻¹) | 10 |
| Reactor system volume (dm ³) | 17–18 |
| Oxygen flow rate (dm ³ min ⁻¹) | 0.005–0.2 |
| Reactor temperature (°C) | 50 |
| Reactor pressure | 1.0 |
| UV lamp power (kW) | |
| Reactor X | 1 |
| Reactor Y | 2 |

operating units. The top section consists of a gas–liquid mixing zone of 0.05 m diameter and 0.5 m long QVF glass tube with a metal cap fastened at the apex. A 5 mm orifice plate is attached to the underside of the cap. Aqueous pollutant and suspended catalyst and oxidant feed (pure oxygen or compressed air or ozone) are mixed in a unique ‘T’ configuration before entering co-currently through the orifice into the fully flooded column. In the fully flooded column, efficient gas–liquid mass transfer is achieved due to the energy and turbulence introduced by the high velocity gas–liquid jet. A close approach to equilibrium of the gas and liquid phase (approximately 97%) is characteristic of this section of the reactor [3,4].

The lower section of the reactor is the photocatalytic reaction zone. This lower section is a 0.65 m long and 0.1 m diameter QVF glass section. The centre of the reaction zone is fitted with a 1 kW UV lamp tube or 2 kW UV lamp tube which is encased by a quartz sheath of 0.05 m diameter and about 0.5 m length. This reaction zone volume was 4.0 dm³ and all couplings joining the glass components were standard QVF type. The reservoir top plate (cover) consists of openings through which TiO₂ and other additives are introduced into the reactor. The liquid stream is re-circulated with the aid of a centrifugal pump. The reactor temperature is monitored by a thermocouple inserted into the top section of the reaction zone through the CDC cap.

The total reactor system volume is 18 dm³; however, in this research the volume of solutions treated was kept at 15 dm³ throughout. Table 1 shows the principal operating parameters of the CDC photocatalytic reactor.

2.2. Experimental procedures

Suspensions were prepared in deionised water by mixing TiO₂ with appropriate solutions of 2,4,6-TCP to give the desired initial concentration of 120 mg dm⁻³. This concentration was selected to represent the behaviour of the photoreaction in a range relevant for contaminated drinking waters (>0.5 ppm). Irradiation commenced after the suspensions had been equilibrated in the dark for 30 min with constant mixing and oxygen sparging. The time, temperature and pH were recorded. Samples were also taken from the reactor effluent subsequently (0.02 dm³) at 15 min interval and temperature and pH were

recorded with corresponding concentration and TOC measured by HPLC and TOC analyser, respectively. The pH of the solution was unaltered; no buffer or other agents were added to control the pH, except in those experiments to investigate the effect of pH that sodium hydroxide or sulphuric acid were used to alter the pH. Temperature was kept constant using cooling water flowing through the cooling coil inserted into the reservoir. The samples were filtered using 0.45 μm nylon filters to remove the catalyst.

2.3. Analysis

The degradation of 2,4,6-TCP was followed using an Agilent 1100 series HPLC operated in isocratic mode under the following conditions: methanol–water (80%:20%); flow rate 1 ml min⁻¹; temperature 25 °C; Column Phenomenex Luna 10 μ Phenyl-Hexyl, 4.6 mm × 250 mm; detector UV at 254 nm; injection volume 5 μL. The course of mineralization of 2,4,6-TCP to carbon dioxide was monitored by a Shimadzu TOC-5050A with ASI-5000A auto-sampler.

2.4. Light intensity and photon flux

Light intensity at various positions in the reaction (irradiation) zone was measured with a spectrometer (Horiba Jobin Yvon, Edison, NJ, SPEX 1680 double spectrometer with 5 nm bandwidth. Spectral response was from 200 to 400 nm and with a 365 nm peak.

2.5. Catalyst characterization

The catalyst, VP Aeroperl P25/20, was supplied by Degussa (70%:30% anatase to rutile; average particle size approximately 20 μm, tapped density 700 mg l⁻¹). It was characterised using dynamic vapour sorption (DVS-1 automated gravimetric vapour sorption analyser, Surface Measurement System Ltd.) giving specific surface area 46.06 ± 15 m² g⁻¹ and surface energy 80.12 mJ m⁻². This instrument measures gravimetric uptake and loss of vapour on the substrate using Cahn D200 recording ultra-microbalance with a resolution of ±0.1 μg.

3. Results and discussion

Total degradation and mineralization of 120 mg dm⁻³ of 2,4,6-TCP solutions was achieved in the CDCR when using a 1.0 kW UV lamp in very short irradiation times (180 min) under optimized reaction conditions (50 °C, 0.01% (w/w) catalyst loading, 0.1 dm³ min⁻¹ oxygen flow rate, 10 dm³ min⁻¹ liquid circulation rate and natural pH). Fig. 2 shows 100% conversion and mineralization (TOC conversion) of 2,4,6-TCP under optimized reaction conditions while Fig. 3 shows a typical degradation course of 2,4,6-TCP under non-optimized reaction conditions leading to 97.95% conversion in 240 min. To achieve an optimized condition for photocatalytic degradation and mineralization of 2,4,6-TCP, the influence of the following variables on the photocatalytic degradation of 2,4,6-TCP were investigated and their best conditions for reaction established.

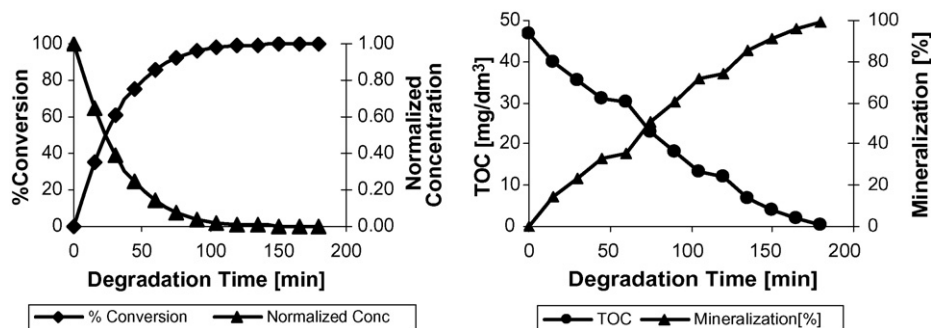


Fig. 2. 100% conversion and mineralization of 2,4,6-TCP under optimized conditions: temperature 50 °C, TiO₂ loading 0.01% (w/w), natural pH, O₂ flow rate 0.1 dm³ min⁻¹, TCP initial concentration 120 mg dm⁻³.

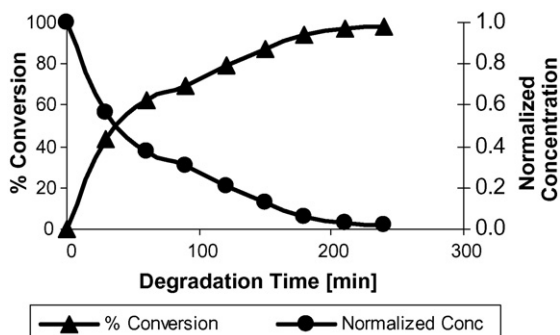


Fig. 3. Degradation of 2,4,6-TCP under non-optimal reaction conditions: catalyst loading 0.03% (w/w), temperature 30–32 °C, natural pH, oxygen flow rate 0.05 dm³ min⁻¹, TCP initial concentration 120 mg dm⁻³.

3.1. Effect of catalyst loading

Fig. 4 shows the effect of photocatalyst loading on the rate of degradation of 2,4,6-TCP using the CDCR. Six catalyst loadings were used in this study (0.005%, 0.01%, 0.03%, 0.05%, 0.07% and 0.1% (w/w)). Optimum loading is required for a given UV source and reactor. A high TiO₂ loading may increase the amount of UV light scattering and hence the interaction between photons and photocatalyst due to an increased extinction coefficient, subsequently reducing the reaction efficiency. On the other hand, a photocatalyst loading which is too low may lead to an insufficient concentration of catalytically active sites for photocatalytic oxidation to proceed at any rapid rate. As a result,

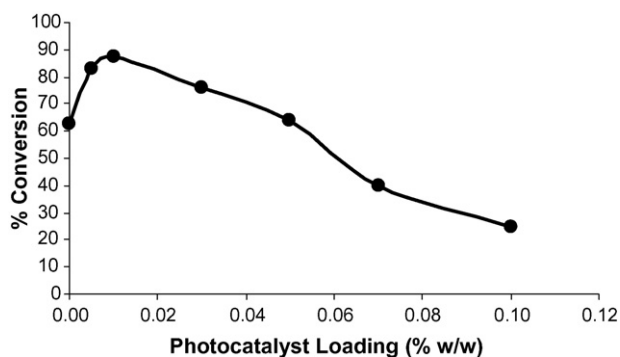


Fig. 4. Effect of photocatalyst loading on 2,4,6-TCP degradation: Reactor X, initial concentration 120 mg dm⁻³, O₂ flow rate 0.05 dm³ min⁻¹, natural PH, time 60 min, temperature 40–50 °C, UV lamp 1 kW.

optimum catalyst loading is dependent upon the reactor configuration, type of pollutant and contact between irradiation source and suspended photocatalyst. This study suggests that 0.01% (w/w) (0.1 g dm⁻³) Degussa VP Aeroperl P25/20 is the optimum photocatalyst loading for the 1.0 kW reactor. Fig. 4 also shows that some 2,4,6-TCP degradation (62.5%) may be achieved in the absence of a photocatalyst. This result suggests that degradation of organic pollutants may also be achieved using UV alone or using UV in combination with oxidizing agents.

3.2. Effect of operating temperature

The dependence of photocatalytic degradation rate on temperature is depicted by the activation energy. This dependency is expressed in terms of Arrhenius' law $k = k_0 e^{-E/RT}$ where k_0 is the frequency factor, E the activation energy of the reaction, R the gas constant, and T is the temperature. The activation energy E , obtained from an Arrhenius type plot (Fig. 5B) was found to be 19.98 kJ mol⁻¹ and this is in accord with the reported value of 20 kJ mol⁻¹ from the work of Chen and Ray [1]. The overall degradation of 2,4,6-TCP at 28, 40 and 50 °C were 98.1, 99.85 and 99.83, respectively, showing an insignificant effect. The degradation profiles (Fig. 5A) shows an exponential decay depicting a first order reaction kinetics typical of most photocatalytic oxidation reactions. The overall influence of temperature is quite insignificant and contrary to thermal reactions, there is no need to heat the system. And since the temperature rises to 50 °C due to the pump action and heat generated by the UV lamp, this temperature was chosen as optimal and used for other experiments. The absence of heating is very attractive for photocatalytic processes. The activation energies reported above are close to that of a hydroxyl radical reaction [1] suggesting hydroxyl radical reaction as the governing factor in the photocatalytic degradation of 2,4,6-TCP.

3.3. Effect of UV lamp power

The effect of UV lamp power on the rate of photocatalytic degradation of 2,4,6-TCP was investigated by experiments using 1 kW UV lamp (X) or 2 kW UV lamp (Y), all other reaction conditions remaining the same. From the results (Fig. 6), with an initial TCP concentration of 100 mg dm⁻³, after 15 min, overall degradation was 33.23% and 71.95% for

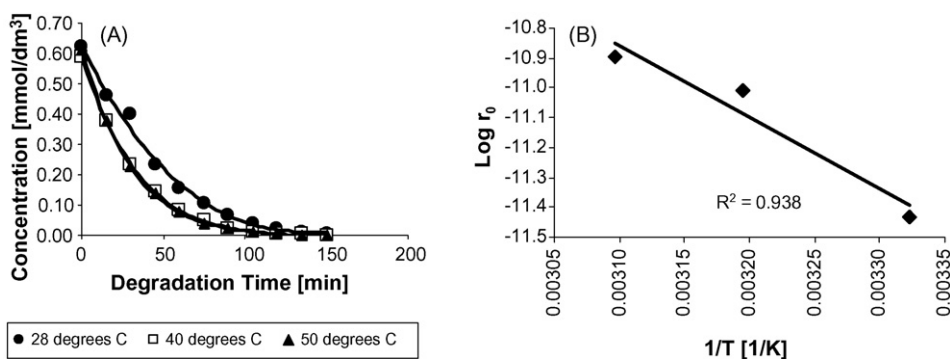


Fig. 5. (A) Effect of operating temperature on 2,4,6-TCP degradation rate; (B) Arrhenius plot.

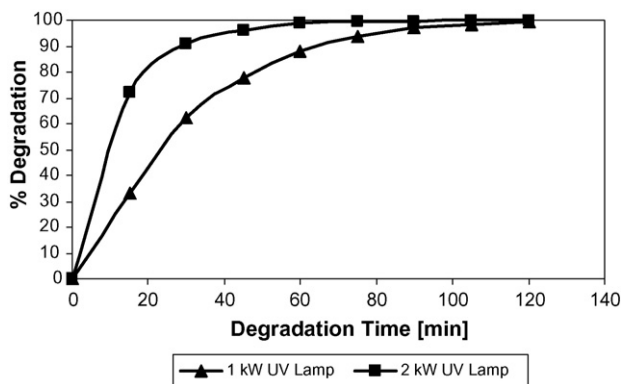


Fig. 6. Effect of UV lamp power on 2,4,6-TCP degradation: temperature 50 °C, photocatalyst loading 0.01% (w/w), O₂ flow rate 0.1 dm³ min⁻¹, initial TCP concentration 100 mg dm⁻³, natural pH.

the 1.0 kW lamp and 2.0 kW lamp respectively, while initial reaction rates 1.3342×10^{-5} and 4.2175×10^{-5} mol min⁻¹, respectively, showing that lamp power has significant effect on the rate of photocatalytic degradation of 2,4,6-TCP. Also, after 30 min, TCP degradation by Reactor Y was 90.71% in comparison with 62.51% degradation by Reactor X, showing significant difference in reaction rate.

3.4. Effect of different UV processes

The effect of different processes is shown by Fig. 7. From the results, the percentage degradation of 2,4,6-TCP by the pro-

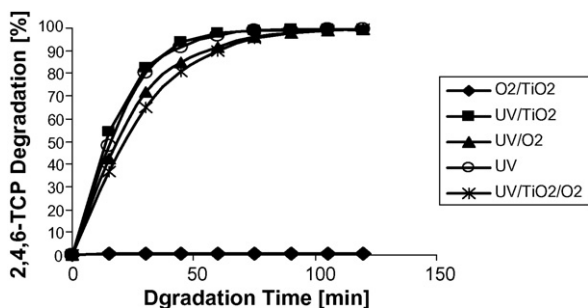


Fig. 7. Effect of different reaction processes on 2,4,6-TCP degradation: catalyst loading 0.01% (w/w), initial TCP concentration 120 mg dm⁻³, Reactor X, UV lamp 1 kW.

cesses TiO₂/O₂, UV/TiO₂, UV/O₂, UV, UV/TiO₂/O₂ after a time window of 120 min are 0.69%, 99.11%, 99.27%, 99.43%, and 99.51%, respectively. From an environmental perspective, mineralization (TOC reduction) may be more important than just the degradation (break down) of the initial organic substrates, as intermediates of degradation may be refractory to further oxidation. More so, the disappearance of the initial organic substrates does not necessarily mean a reduction in the overall hazard of the water or wastewater. The use of TiO₂/O₂ was inefficient in degrading TCP. When UV alone was used, intermediates formed were more prominent and refractory even though 99.43% of the initial TCP was degraded. When combinations including UV were used, over 99% of the initial TCP was degraded in comparison with 0.69% degradation by the TiO₂/O₂ within the same time window of 120 min. This clearly indicates that UV alone is a very efficient process for the breakdown of the TCP and hence other organic compounds. However, the intermediates formed when UV, UV/TiO₂, UV/O₂ were used were more refractory in comparison with the rapid breakdown to final products (CO₂, H₂O and HCl) when UV/TiO₂/O₂ process was used [4].

3.5. Effect of initial concentration of 2,4,6-TCP

This study concentrates mainly on the use of initial TCP concentrations of 120 mg dm⁻³, but some studies were conducted using 65, 500 and 1054 mg dm⁻³ to assess the effect

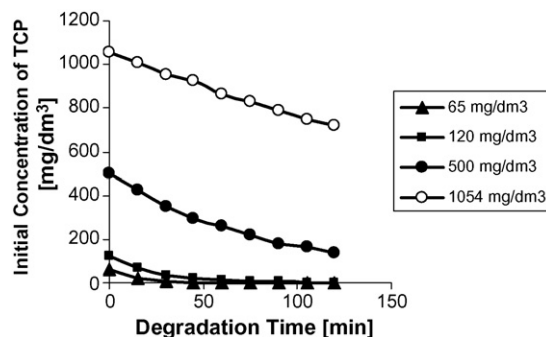


Fig. 8. Effect of initial concentration on 2,4,6-TCP degradation: Reactor X, catalyst loading 0.01% (w/w), natural pH, time 120 min, UV lamp 1 kW.

of initial organic substrate concentration on the degradation rate. In photocatalytic oxidation of organic pollutants, reaction rate depends on light intensity, dissolved oxygen concentration and initial concentration of the organic substrate. Using low initial TCP loading (65 mg dm^{-3}), 100% conversion of the pollutant was achieved in 120 min while 99.58% conversion was achieved in 120 min when 120 mg dm^{-3} was used. When 500 and 1054 mg dm^{-3} initial TCP loadings were used for the same time window of 120 min, conversions were 72.50% and 31.69%, respectively. For the higher initial concentrations, total degradation would have been achieved with longer irradiation times. Fig. 8 show these results.

4. Conclusion

Results have shown that the pilot scale CDCR equipped with a 1.0 or 2.0 kW lamp is capable of total degradation and mineralization of 2,4,6-TCP showing promise for industrial scale treatment of wastewater. The very high mass transfer efficiency and mixing achievable in the CDCR aids photocatalytic reaction and enables reaction to occur in very short irradiation times. Under optimized reaction conditions, 100% conversion of 2,4,6-TCP was achieved in 180 min using 15 dm^3 solutions with initial concentration of 120 mg dm^{-3} . A combination of TiO_2 photocatalyst, UV irradiation and oxidant was observed to give the most rapid photodegradation and photomineralization of the 2,4,6-TCP in comparison with irradiation only. Using the 1 kW or 2 kW UV lamps, conversion of 100 mg dm^{-3} of 2,4,6-TCP after 30 min was 62.51% and 90.71% with initial reaction rates of 1.33×10^{-5} and $4.22 \times 10^{-5} \text{ mol min}^{-1}$ and rate constants of 0.0046 and 0.29 min^{-1} , respectively.

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