

The effect of pH on UV-based advanced oxidation technologies – 1,4-Dioxane degradation

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ABSTRACT

1,4-Dioxane, is a synthetic organic compound used widely throughout industry as a solvent. 1,4-Dioxane causes liver damage and kidney failure and has been shown to be carcinogenic to animals, and is a potential carcinogen to humans. Its recalcitrant nature means that conventional water treatment methods are ineffective in removing it from water. A class of technologies called advanced oxidation technologies has been shown to completely mineralise 1,4-dioxane. In this study the effects of pH on TiO₂ photocatalysis reactor systems were investigated. pH was found to significantly affect the efficiencies of these processes with neutral pH conditions the most effective.

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1. Introduction

1,4-Dioxane (C₄H₈O₂, CAS No. 123-91-1) is a cyclic organic compound. Its two oxygen atoms make it hydrophilic and infinitely soluble in water (aqueous solubility = 4.31×10^{-5} mg/L). It is recalcitrant to microbial degradation and its low estimated soil sorption partition coefficient make 1,4-dioxane highly likely to leach to groundwater [1]. 1,4-Dioxane is directly used as a solvent stabiliser, and wetting and dispersing agent and as an unwanted by-product in the manufacture of polyethylene terephthalate (PET) plastic and ethoxylated chemicals, in particular surfactants [2]. The wide and frequent use of 1,4-dioxane in industrial processes and consumer products, combined with its biological recalcitrance and high solubility has led to the contamination of soils, surface water, ground water, and wastewater in countries where the chemical has been used. It has been detected in water samples in the UK, Canada, Japan and in various locations in the US [1,3]. In Australia, although the presence of 1,4-dioxane in water bodies has not been detected, an environmental risk assessment [2] predicted that the majority of 1,4-dioxane used and produced as a by-product is released to sewer. The majority of contamination is due to landfill leachate from landfills containing radioactive waste, waste plastic residue from manufacturing plants and from 1,1,1-trichloroethane contaminated groundwater and chemical and municipal plant effluents [3].

1,4-Dioxane is classified by the United States Environmental Protection Agency (U.S. EPA), the International Agency for Research on Cancer (IARC) and the Agency for Toxic Substances and Disease Registry (ATSDR) as a probably human carcinogen. Insufficient data is available to access the carcinogenicity of 1,4-dioxane to humans. However, animal studies have shown that 1,4-dioxane does result in cancers. Replicated exposure of 1,4-dioxane administered in drinking water resulted in liver and nasal cavity tumours in rats, liver carcinomas and adenomas in mice and liver and gall bladder tumours in guinea pigs [4]. 1,4-Dioxane was declared a Priority Existing Chemical in Australia on 3rd May 1994 due to concerns of carcinogenicity, its potential for widespread occupation and public exposure and high degree of partitioning to, and persistence in the aquatic environment [2].

Conventional water treatments have proven ineffective in the removal of 1,4-dioxane from contaminated water. Physical methods including carbon adsorption and air stripping are not feasible or cost effective due to the high aqueous solubility and low vapour pressure of 1,4-dioxane [5]. Distillation is physically viable, but 1,4-dioxane's high boiling point (bp = 101 °C) makes the separation and removal process extremely energy intensive, and thus uneconomical for most applications [6]. Chemical treatments such as chlorination are an option; however chlorination by-products are more toxic than 1,4-dioxane [5]. Advanced oxidation processes that utilise UV light to initiate the formation of hydroxyl radicals offer faster removal rates of 1,4-dioxane from solution. 1,4-Dioxane is characterised as a very weak absorber of UV light, and hence degradation by direct photolysis is unlikely [3]. However, in the presence of hydroxyl radicals produced by direct photolysis of hydrogen per-

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oxide or TiO₂ as a photocatalyst [7,8], 1,4-dioxane decays rapidly following first order kinetics [9,10]. Coleman et al. [8] reported that a slurry reactor using commercial P25 TiO₂ photocatalyst with UVA light ($\lambda_{\max} = 350$ nm) to be 15 times more effective than the 3 ppm H₂O₂/UVC ($\lambda_{\max} = 254$ nm) process. Different reactor systems using TiO₂ are under investigation [8] and include slurry, immobilised [11] and sol–gel systems [12]. Light intensity and wavelength play an important role in the efficiency of photocatalytic systems. It is important to match the absorbance of the chemical involved in the production of hydroxyl radicals. For TiO₂ a wavelength no shorter than 390 nm is required in order to produce the electron–hole pairs that initiate reaction and degradation mechanisms. In the degradation of 1,4-dioxane using a TiO₂ photocatalyst UVA light is more efficient than solar [10].

Hill et al. [7] reported complete mineralisation of 1,4-dioxane in aqueous solution by the combined action of light ($A > 300$ nm) and TiO₂. Ethylene glycol diformate (EGDF, also known as 1,2-ethanediol diformate) was found to be the most significant observable intermediate [7]. Similar studies of heterogeneous photocatalysis have also revealed EGDF as the principal oxidation by-product along with minor amounts of formaldehyde and formic, glycolic and oxalic acids [13–16]. Acetic acid and β -hydroxybutyric acids were also reported by Mehrvar et al. [14,15]. It is speculated that 1,4-dioxane-2,3-diol and [1,2-ethanediylbis(oxy)]bis[methanol] are also 1,4-dioxane intermediates [14].

There are limited and mixed reports on the effect of pH on degradation of 1,4-dioxane in water. Increased degradation on TiO₂ photocatalysts have been reported both for alkaline and acidic conditions. Coleman et al. [17] used pH 3 for 1,4-dioxane degradation whilst Maurino et al. [13] reported 1,4-dioxane disappearance to be greater at pH 11 than at pH 5.5 although the reverse was observed for total organic carbon (TOC) decreases. This indicates that further degradation of organic intermediates exhibiting a negative charge at pH 11 (e.g. carboxylic acids) is inhibited at $\text{pH} > \text{pH}_{\text{zpc}}$ of the catalyst. Degradation intermediate products also may change at different pH values. For example, ethylene diamine tetra acetic acid (EDTA) was observed at pH 11 as opposed to EGDF at lower pH values in 1,4-dioxane degradation [13,15]. Lam et al. [16] found that the photocatalytic oxidation of 1,4-dioxane at pH 3 involved a two-step reaction controlled by the degradation of EGDF. Whilst at pH 5 a more complex process was involved.

Therefore, the main aim of this paper is to investigate the effects of pH to optimize the removal of low concentrations of 1,4-dioxane in water for three different TiO₂ photocatalytic reactors: slurry P25, sol–gel and P25 immobilised reactor systems.

2. Experimental

2.1. Chemicals

1,4-Dioxane was obtained from Riedel-de-Haen (99%) and used as received. Aqueous stock solutions were prepared weekly in deionised water obtained from a Millipore® Milli-Q water system. Perchloric acid (70%, Ajax Chemicals), sodium hydroxide (Chem Supply), and titanium dioxide (Degussa-P25) were used as supplied.

2.2. Reactor set-ups

Photocatalytic experiments were carried out using a batch spiral reactor (volume = 50 mL) constructed using borosilicate glass tubing of 6 mm outer diameter and 1 mm wall thickness with titanium dioxide either in suspension or immobilised to the inside wall of the reactor. Two different methods to immobilise TiO₂ were used. The first method used the sol–gel process and was based on a method

by Hong [12]. This involved the addition of the solvent isopropanol (23 mL), to titanium tetra isopropoxide (50 mL) under gentle stirring, before the drop-wise addition of further isopropanol (23 mL) that had been mixed with water (1.5 mL). This sol–gel solution was then refluxed for 24 h in a water bath set at 78 °C under constant stirring until clear and golden yellow. The solution was then pumped slowly through the spiral reactor under controlled humidity levels set at 2%, and left for 5 min to allow the formation of a thin coating on the walls of the reactor before being pumped out. Drying for 2 h at 120 °C followed prior to calcination at 400 °C for 1 h to complete the process. This reactor is referred to as the TiO₂ Sol–gel reactor. The second immobilisation method was based on a method by Abdullah et al. [11] and involved filling the reactor with 20% hydrofluoric acid for 1 h to etch the inside surface of the reactor. 1% P25 TiO₂ (sonicated in an ultrasonic bath for 20 min) was then pumped through and allowed to stand for approximately 1 h before being dried in a 60 °C oven. This process was repeated 3–4 times to form a film of TiO₂ on the inside wall of the reactor referred to as the immobilised P25 reactor. A UVA light source (NEC, 20 W, $\lambda_{\max} = 350$ nm) was fitted through the centre of the spiral reactor coil and a peristaltic pump (Masterflex® Quick-Load, Cole-Palmer Instrument Co.) connected to the reactor by Masterflex tubing enabled a solution flow rate of 465 mL/min to circulate. A schematic of the reactor set-up is shown in a previous publication [17].

2.3. Experimental procedure

50 mL of 1 g/L TiO₂ suspension (sonicated for 30 min) with the pH adjusted using either perchloric acid or sodium hydroxide was added to the reactor. The suspension was irradiated with a UVA lamp for 30 min to mineralise any organic impurities, before a 10 min air-equilibration period. The UVA lamp was then switched off and 1,4-dioxane was added to achieve an initial concentration of 36 ppm of 1,4-dioxane in solution. This was left to mix for 10 min before the light was switched on to commence the experiment (time = 0 min), and left on for the duration of the experiment. Samples were collected intermittently and filtered through 0.45 μm filters (Sartorius, Minisart SRP 25) to remove the suspended P25 particles prior to total organic carbon (TOC, Shimadzu TOC-V_{CSH}) and high performance liquid chromatography (HPLC, Waters 2695) analysis. A C18 Atlantis® column (4.6 mm \times 250 mm) was utilised to perform the separation. The mobile phase consisted of 95% water and 5% acetonitrile and this was maintained at a 1 mL/min flow rate. Detection and monitoring occurred for two chemical species; 1,4-dioxane ($\lambda = 200$ nm, retention time, $t_r = 6.6$ min) and the main intermediate product ethylene glycol diformate ($\lambda = 208.5$ nm, $t_r = 7.7$ min).

This procedure was used for all experiments except pH adjusted milli-Q water was added to the reactor system instead of the TiO₂ suspension. The mineralisation of 1,4-dioxane was monitored by TOC analysis at intervals during the reaction, and for experiments at pH 3 by solution conductivity detected by an online 4510 Jenway Conductivity Meter.

3. Results and discussions

3.1. Dark adsorption and UVA light alone

No removal of 1,4-dioxane occurs with titanium dioxide in the dark indicating negligible adsorption of 1,4-dioxane on TiO₂. Also insignificant degradation of 1,4-dioxane was observed (<15% over an irradiation period of 2 h) in the presence of UVA light alone.

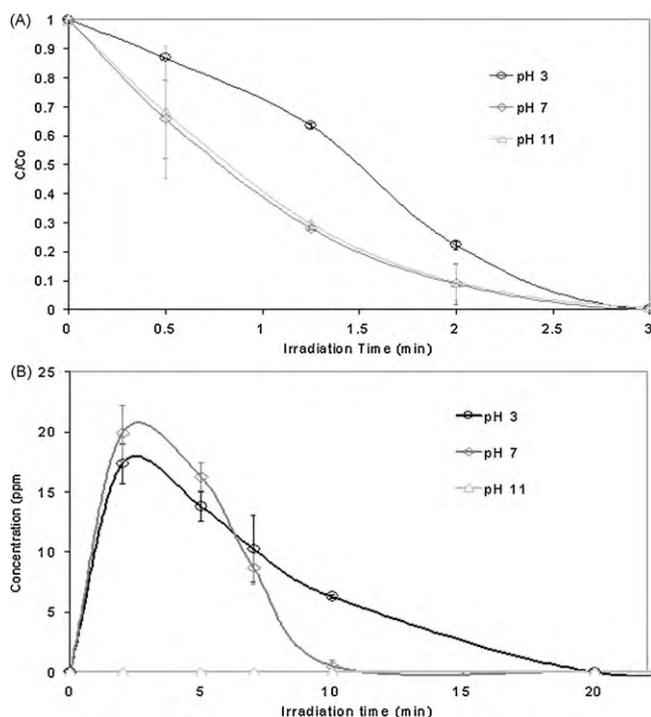


Fig. 1. 1,4-Dioxane degradation (A) and EGDF formation and degradation (B) in a P25 slurry reactor system with UVA light.

Table 1
Initial rate constants (min^{-1}) for 1,4-dioxane degradation in a P25 slurry reactor system and UVA light.

P25 slurry	pH 3	pH 7	pH 11
Rate constant (min^{-1})	0.73 ± 0.03	1.48 ± 0.46	1.20 ± 0.32

3.2. Titanium dioxide photocatalysis

3.2.1. P25 slurry photo-reactor system

The results for photocatalytic degradation of 1,4-dioxane in water at three different pH values; pH 3 (acidic), pH 7 (neutral) and pH 11 (alkaline) using a P25 slurry photo-reactor system and UVA light are shown in Fig. 1A. At all three pH values complete removal of 1,4-dioxane was obtained within 3 min. 1,4-Dioxane removal was similar for pH 7 and 11, both occurring faster than at pH 3. First order reactions were observed and the first order initial rate constants (see Table 1) confirm the degradation order of pH 7 and 11 to be greater than at pH 3.

1,4-Dioxane removal at pH 3 was the slowest, $0.73 \pm 0.03 \text{ min}^{-1}$, as indicated in Fig. 1A. The surface charge of titanium dioxide has been proven to be highly pH dependent changing its adsorption mode and the distribution of hydroxyl radicals [18]. Hydroxyl radical formation has been postulated to be the primary mechanism in photocatalytic oxidation [19]. The point of zero charge (pzc) of TiO_2 is 6.3–6.8 [18,19]. At pH 7 which is close to the pzc of TiO_2 , the catalyst would have no charge, possibly allowing molecules to easily reach the catalyst surface and achieve higher initial reaction rates. Complex electrostatic interactions could be occurring between the molecules and the catalyst in acidic and alkaline conditions that reduce 1,4-dioxane removal. However, at alkali pH the surface of the TiO_2 is highly hydroxylated [21], which would enhance the overall reaction and thus offer a reason why a reduced 1,4-dioxane removal similar to pH 3 was not observed. Competition for hydroxyl radicals by carbonate ions (CO_3^{2-}) may offer a possible explanation why degradation was not fastest at pH 11. When complete mineralisation of 1,4-dioxane occurs carbon dioxide, mineral acids and

water are formed. At pH 11, carbonic acid would dissociate to the carbonate ion (CO_3^{2-}). Carbonate ions have been shown to be radical scavengers, reacting with hydroxyl radicals to produce the less reactive carbonate radical ($\text{CO}_3^{\cdot-}$) [22]. Mehrvar et al. [22] found that the presence of carbonate ions as a radical scavenger slows down the degradation of 1,4-dioxane. It is also worth noting that perchloric acid which was used to adjust pH values has not been found to influence photocatalytic reactions [20].

For all pH values displayed in Fig. 1A the initial degradation rate constants for the disappearance of 1,4-dioxane reduced as time progressed. This could be due to competition for hydroxyl radicals by intermediates (e.g. ethylene glycol diformate) formed as a result of 1,4-dioxane degradation. As time progresses, there would be greater concentrations of intermediates and less 1,4-dioxane molecules present in solution. Thus, the probabilities of 1,4-dioxane molecules reacting with hydroxyl radicals would be reduced.

The levels of ethylene glycol diformate (EGDF), the main intermediate of 1,4-dioxane degradation [7,13,15,16], were also monitored throughout the irradiation period by HPLC analysis and are shown in Fig. 1B. EGDF was detected at both pH 3 and 7, but no EGDF was detected at pH 11. Formation of EGDF is slightly faster and concentrations greater at pH 7 compared to pH 3. In addition, EGDF is degraded much faster at pH 7 than at pH 3. This agrees well with Lam et al. [16] who found that the photocatalytic degradation and mineralisation of EGDF was more superior at pH 5 than at pH 3, most likely due to reaction kinetics. The presence of EGDF at pH 3 and 7 indicates that the same oxidative ring opening mechanism was used for 1,4-dioxane degradation. At pH 11 either a different mechanism was used, or EGDF was produced but was degraded so quickly via a different mechanism to that of pH 3 and 7 that it was not detected. Maurino et al. [13] also reported no EGDF was detected at pH 11 and conducted separate experiments to find EGDF was quickly hydrolysed to ethylene glycol and formate in dilute aqueous solutions at $\text{pH} \geq 11$ (>95% in 90 s). This was different to the small quantities of ethylene glycol, and relatively large amounts of formaldehyde, glycolaldehyde, formic and glycolic acids detected at pH 5.5. Different reaction pathways were proposed to explain their findings. Mehrvar et al. [14] also detected and identified EGDF, formaldehyde and formic, glycolic and oxalic acids as intermediates during the photocatalytic oxidation of 1,4-dioxane at pH 4.

A small drop in pH was observed at the end of photocatalytic oxidation experiments for the P25 slurry system. The acidic intermediate products of 1,4-dioxane mentioned above could account for this observation. Suh and Mohseni [6] also observed that the formation of oxidation intermediates was evident from the gradual decline in the pH of the solution for all photocatalytic experiments.

3.2.2. TiO_2 sol-gel photo-reactor system

Photocatalytic oxidation of 1,4-dioxane was performed at two different pH values; pH 3 (acidic), pH 7 (neutral) using the TiO_2 sol-gel photo-reactor system and UVA light as described in Section 2.3. A comparison at pH 11 for the sol-gel system was not possible due to the fact that the coating is unstable under alkaline conditions. Fig. 2A indicates that 1,4-dioxane is completely degraded both at pH 3 and 7, with no detectable amounts of 1,4-dioxane at 60 min and 45 min, respectively. This trend agrees with the results obtained at pH 7 for the P25 slurry system where 1,4-dioxane also degraded at a faster initial rate. First order initial rate constants confirm this being $0.07 \pm 0.001 \text{ min}^{-1}$ and $0.11 \pm 0.009 \text{ min}^{-1}$, respectively, pH 7 being 1.6 times faster than pH 3 (Table 2).

The EGDF profile (Fig. 2B) exhibits an almost identical trend to that in the P25 slurry EGDF profile. This factor, plus similar 1,4-dioxane profiles and ratios of initial rate constants for each pH, indicate that the same mechanisms and similar reaction kinetics discussed in Section 3.2.2 is responsible for the difference in the

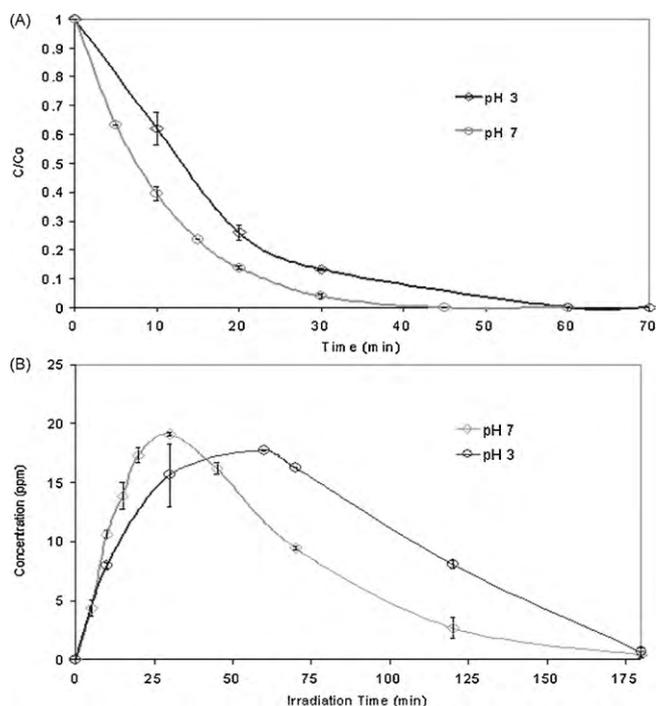


Fig. 2. 1,4-Dioxane degradation (A) and EGDF formation and degradation (B) at pH 3 and 7 using a TiO₂ sol-gel reactor system and UVA light.

Table 2

Initial rate constants for TiO₂ sol-gel reactor system and UVA light.

TiO ₂ sol-gel reactor	pH 3	pH 7
Rate constant (min ⁻¹)	0.07 ± 0.001	0.11 ± 0.009

initial degradation rates of 1,4-dioxane and EGDF observed for pH 3, 7 and 11, and this occurs independent of reactor design.

3.2.3. Photocatalytic reactor design

Three different titanium dioxide systems were tested at pH 7 which is the pH found to achieve higher initial degradation rates and where less complex reaction kinetics could be occurring due to the surface charge of the catalyst being close to neutral. The systems include the P25 slurry photo-reactor, immobilised P25 photo-reactor, and the TiO₂ sol-gel photo-reactor system with UVA light as described in Section 2.2. All three reactor systems resulted in the complete degradation of 1,4-dioxane. 1,4-Dioxane initial degradation rates were found to be first order for all three systems. The initial first order rate constants are shown graphically in Fig. 3.

The P25 slurry system is the fastest system for 1,4-dioxane degradation being 2.6 times faster than the P25 immobilised system and 13.7 times faster than the TiO₂ sol-gel reactor system. A similar trend was observed by Coleman et al. [8,10] for mineralisation of 0.36 ppm 1,4-dioxane at pH 3 where a P25 slurry reactor was 6 times faster than a sol-gel reactor. The main difference between the P25 slurry system and the other two systems mentioned is that the P25 photocatalyst is in suspension and not immobilised on the inside walls of the reactor. The high surface area available for photocatalytic reactions in comparison to the two immobilised systems would account for the main reason for the large difference in initial reaction rates observed. The P25 slurry system also has reduced mass transfer effects that are pertinent in the other systems. Despite the P25 slurry system exhibiting the highest initial degradation rates, the immobilised systems offer greater practicality for industrial applications as they eliminate the costly filtration and separation steps needed to remove the suspended catalyst.

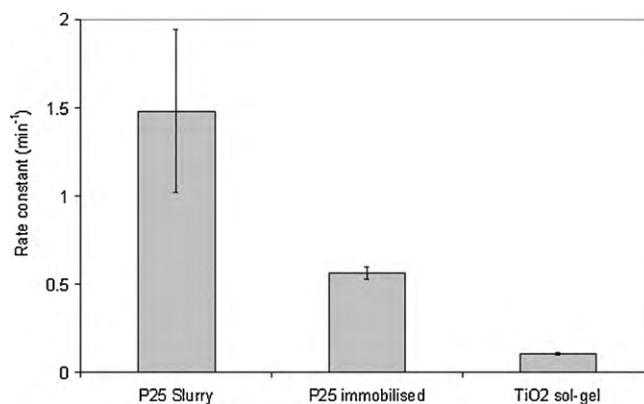


Fig. 3. First order initial rate constants for 1,4-dioxane degradation in the P25 slurry, the P25 immobilised and the TiO₂ sol-gel photocatalytic reactor systems with UVA light at pH 7.

The P25 immobilised system was found to degrade 1,4-dioxane 5.2 times faster than the TiO₂ sol-gel reactor system. As both are immobilised systems, the difference in initial reaction rates can be attributed to the different characteristics of the titanium dioxide. P25 (Degussa) is a well-known highly photoactive commercial catalyst whose properties are maximised for photocatalytic oxidation (70% anatase, 30% rutile) [15]. The photo-generated holes and electrons of the anatase form of TiO₂ have been reported to be highly oxidising and reducing, respectively, much greater than that of the rutile phase [24]. However, the presence of the rutile phase is reported to enhance the activity of the anatase phase by serving as an electron sink [25]. Anatase to rutile transformation is expected to take place between 700 °C and 800 °C [26]. As 400 °C was the maximum temperature used to create the TiO₂ sol-gel reactor (see Section 2.2), it can be assumed that no rutile phase was formed and why increased initial degradation rates were not observed. Another possible reason could be attributed to a decline in surface area (due to sintering and crystal growth) and a loss of surface hydroxyl groups [27], due to the temperatures used in the calcination step of the sol-gel process.

The EGDF formation and degradation profile for each of the different systems is shown in Fig. 4. The results show the same order of reactivity as seen for 1,4-dioxane degradation, thus re-affirming that EGDF formation is a direct result of 1,4-dioxane degradation and that all three systems have similar reaction mechanisms taking place initiated by the hydroxyl radical.

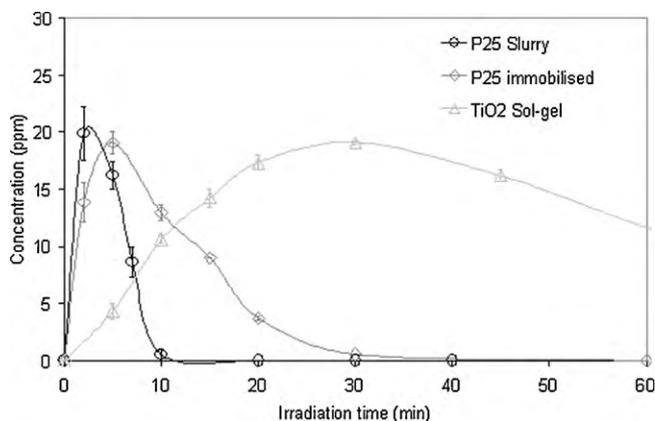


Fig. 4. EGDF formation and degradation profiles for the P25 slurry, P25 immobilised and the TiO₂ sol-gel systems in UVA light.

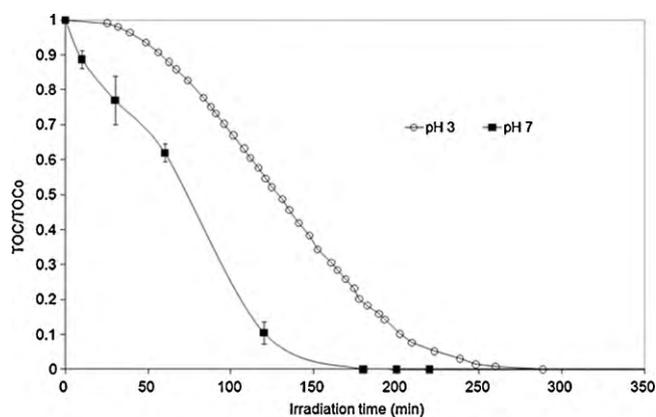


Fig. 5. Carbon profile for 1,4-dioxane degradation using a TiO₂ sol-gel reactor and UVA light at pH 3 and 7.

3.2.4. Mineralisation studies

One of the major benefits of advanced oxidation processes is the potential for organic compounds to be completely oxidised to carbon dioxide and water, leaving no possible harmful intermediates. Although 1,4-dioxane and EGDF concentration levels were monitored during the reaction process, it cannot be concluded from this information alone that all the initial 1,4-dioxane and intermediates formed are completely mineralised to carbon dioxide and water. To confirm complete mineralisation had been achieved TOC measurements were taken at the end of all experiments. Carbon profiles for the TiO₂ Sol-gel and UVA light process at pH 3 and 7, shown in Fig. 5 were also completed. A profile was not completed for pH 11 due to the coating being unstable under alkaline conditions.

Fig. 5 shows a steady decline in the amount of carbon present until no more is detected at around 230 min and 180 min for pH 3 and 7, respectively, both times being about 30 min after the time at which EGDF was last detected. This indicates that further intermediate products are quickly mineralised, that EGDF is the slow step in oxidation of 1,4-dioxane and that a similar degradation pathway is occurring at both pH 3 and 7. This agrees well with Maurino et al. [13], Hill et al. [7], and also with Lam et al. [16] who found that the mineralisation of 1,4-dioxane at pH 3 involved a two-step reaction with the overall performance controlled by the degradation of EGDF.

4. Conclusion

The advanced oxidation technology, titanium dioxide photocatalysis, is effective in degrading 1,4-dioxane in water. pH was shown to have an effect. Not only on the initial reaction rate but on the intermediate products produced. Ethylene glycol diformate was the main intermediate product at pH 3 and 7, but no ethylene glycol diformate was detected at pH 11. Neutral (pH 7) and alkaline (pH 11) conditions produced higher 1,4-dioxane initial degradation rates than acidic (pH 3) conditions. No 1,4-dioxane degradation occurred using a TiO₂ sol-gel reactor system in the dark and UVA light alone had minimal effect on 1,4-dioxane degradation. Mineralisation studies showed complete mineralisation of 1,4-dioxane occurred during the photocatalytic reaction. The time interval between EGDF removal and mineralisation was compared to 1,4-dioxane degradation to confirm that EGDF degradation is the slow step in the complete mineralisation of 1,4-dioxane. The P25 slurry photo-reactor system was more efficient than the immobilised systems due to the higher surface area of catalyst available for reaction. The P25 immobilised system was more effective than the TiO₂ sol-gel photo-reactor system due to the photoactivity of the catalyst.

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