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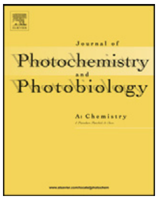

Degradation of oxalic acid in a photocatalytic ozonation system by means of Pilkington Active^{TM} glass

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ABSTRACT

This study aims to present the effect of combined ozone and immobilized TiO_2 in the form of a well-known commercial product, Pilkington Active^{TM}, as a photocatalyst for the degradation of oxalic acid in aqueous solutions which is refractory to conventional ozonation treatments. Inclusive results on the influence of experimental variables such as temperature, pH value and initial concentration of oxalic acid on the rate of oxalic acid degradation and ozone consumption are demonstrated. Total organic carbon analyses were performed to investigate the mineralization of oxalic acid. Due to the enhanced photogeneration of hydroxyl radicals as a consequence of a synergistic interaction between the photo-activated TiO_2 and ozone, the O_3/Pilkington Active^{TM}/UVA system showed excellent potential for the oxidation and removal of oxalic acid contaminants in water.

1. Introduction

Ozone is a very powerful oxidizing reagent ($E^0 = 2.08$ V) which reacts with many groups of organic and inorganic compounds directly and/or indirectly, mainly via the formation of the more oxidant OH radicals ($E^0 = 2.8$ V) [1]. Despite these positive points, ozone, besides high production costs, has a relatively low solubility and stability in water and, furthermore, it reacts slowly with some organic compounds, such as inactivated aromatics and saturated carboxylic acids, and in many cases it does not completely oxidize these organic compounds [2]. These disadvantages make the application of ozone alone in polluted water treatment unfeasible from an economic point of view. Therefore, many studies have focused on the performance enhancement of ozonation systems by combining them with different categories of ions, metal oxides and irradiations [3–5].

Due to the low toxicity and costs, commercial availability, chemical inertness and high photoconductivity of TiO_2, its use in the anatase-rutile form as a photocatalyst in the oxidation and removal of innumerable pollutant chemical compounds in water and air has received an increasing amount of attention in recent years [6–9]. Furthermore, several scientific works in the field of TiO_2 heterogeneous photocatalytic activities in combination with ozone in aqueous solutions to remove different groups of compounds have been reported [10–12]. This photocatalyst generates electron–hole pairs when irradiated with UV/vis light with energy in the range of the TiO_2 band gap, $E_{bg} = 3–3.2$ eV [13]. The active electron (−)–hole (+) pairs handle the redox reactions with various species adsorbed onto the semiconductor surface.

The immobilization of stable TiO_2 films on support materials instead of using such semiconductors in aqueous suspensions solves two significant problems for researchers: first, the difficulties in filtering and recycling the photocatalyst, and second, the extinction of UV light due to scattering and absorption of the radiation by the particles themselves. However, better mass transfer properties and process simplicities are still the most important advantages in slurry applications [14,15].

Oxalic acid is one of the toxic pollutants existing in alumina processing liquors [16] and textile industrial wastewaters [17]; furthermore, oxalate is a detectable intermediate in the mineralization of many pesticides and other organic compounds [18–20] and, at the same time, it is oxidized directly to CO_2 without the formation of any stable intermediate products [21,22]. This compound is recalcitrant to the direct attack of ozone alone, specially at an acidic pH [23]. The four abovementioned properties were the reasons why oxalic acid was chosen as the model compound in our work.

Despite many investigations reporting on the degradation of oxalic acid in aqueous solutions by various treatment systems, there is a lack of studies investigating the degradation behaviour of this compound when a well-known commercial immobilized TiO_2 combined with O_3/UVA is used. Introduction of this commercialized product and assessment of its performance combined

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with ozone and UVA light in degradation of special compounds under different conditions is a new concept might open more doors toward application of such products in the field of water treatment. Therefore, the present paper aims to investigate the synergistic effects among ozone, immobilized TiO_2 in the form of a commercialized product, Pilkington Active^{TM} glass and near UV light, in the degradation of oxalic acid by a heterogeneous photocatalytic ozonation treatment.

2. Experimental details

2.1. Reagents, materials and analyses

The oxalic acid solutions were prepared from Merck (Germany) analytical grade substances. All treatments were performed using pH 2.1 ± 0.1, except for the attempts to show the influence of different pH values on the degradation rate, when NaOH (Lachema, Czech Republic) was used to increment the pH value (pH 3–9 ± 0.1) of the solutions. The pH was measured using a pH-196 Microprocessor pH-meter (WTW, Germany).

The initial oxalic acid concentration for all attempts was 10 mM; while to investigate the concentration effect on degradation rate, oxalic acid solutions of 1–50 mM were treated. Samplings and analyses have been carried out every 20 min in 5 periods of time, so that each treatment has lasted 100 min.

All treatments were performed at 25 °C, except for those in the temperature effects study. The solution temperature was fixed at the required temperatures, 10–70 ± 0.2 °C, using a thermostatic bath (LAUDA model B, Germany).

The Pilkington Active^{TM} glass sheets [24–26] were used as an immobilized photocatalyst after cutting without any further preparation processes.

Oxalic acid concentration measurements were performed by ionic chromatography using the Dionex DX 500 with conductivity detection connected to an Ion Pac AG4A (guard column) and an AS14 anion exchange column with a 4 mm format (Dionex). The samples were pumped through a sample loop at a volume of 100 μl. The flow rate of the mobile phase, $NaHCO_3$ (1.7 mM)/Na_2CO_3 (1.8 mM), was fixed at 1.2 ml/min. The evaluation of the mineralization level of oxalic acid was performed by means of a TOC-5000 Shimadzu (total organic carbon) analyzer (Japan).

The ozone analyzer, Anseros Ozomat GM model RT1 (Germany), measured ozone existing in the gas phase in the ozonation chamber during the process. The ozone consumption level was calculated by comparing the input ozone concentration after reaching the steady state conditions with the output values during treatment. The ozone concentration in the liquid phase was measured by Indigo method [27]. After about 10 min, the equilibrium was achieved between liquid phase and gaseous phase. A maximum ozone concentration of 14 ± 1 mg/l was measured in the liquid phase.

2.2. Installation

The setup details (a) and structure of the planar reactor (b) used in this work are shown schematically in Fig. 1. A Pilkington Active^{TM} glass sheet, 30 cm × 5 cm × 0.5 cm, was embedded and fixed in a polymethylmethacrylate box so that UV light could reach the semiconductor surface easily. After passing through the ozonation chamber the oxalic acid solution was injected through the inlet point at the bottom of reactor to make a thin layer over the photocatalyst surface and it left the reactor through the top outlet point. The solution was transferred to the ozonation chamber to be recycled again. The recycling of oxalic acid solution was performed using a Micropump 75211-15 gear pump. Before sampling was started, the oxalic acid solution was recycled through the reactor in the dark for 10 min by bubbling oxygen into the ozonation chamber in order to achieve steady state conditions. The UV light and the ozone generator were switched on 30 min before connecting to the system for the same reason. More installation details are available in Table 1.

Table 1
Setup and application details.

Photocatalyst surface area	150 cm^2
Thickness of solution over the photocatalyst	3 mm
Ozonation chamber volume	500 ml
Reactor volume	160 cm^3
Solution recycling rate	1 l/min
Solution volume for each treatment	400 ml
Sampling volume	5 ml
Oxygen input flow rate	10 l/h
Input ozone concentration	145 ± 2 mg/l-O_2

A UV lamp (Narva Lichtquellen GmbH & Co. KG, LT 30 W/009) providing a range of wavelengths between 300 nm and 420 nm, and a pronounced maximum wavelength of about 360 nm was used as irradiation source. The light intensity of the UVA light source was ca. 1 mW/cm^2.

The ozone generator (Fischer OZ 502/10, Germany) produced ozone from pure, dry oxygen (Air Liquide, >99.5 vol.%, H_2O <200 ppmv) on demand. The oxygen/ozone mixture input rate was adjusted to 10 l/h (1.45 ± 0.02 g O_3/h or 145 ± 2 mg O_3/l-O_2).

After each attempt, the reactor was washed with 2 l of deionized water and prepared for the next treatment.

3. Results and discussion

The deviation in the results (oxalic acid concentration and ozone consumption level) after reproducing our study was lower than 5%. Table 2 shows the abbreviations used in the illustration of the results.

Before starting the functional assessment of the parameters (initial concentration of pollutant, solution pH value and temperature), a general experimental study was performed to investigate the oxalic acid removal rate under our reactor conditions for six different oxidation systems (Fig. 2). Fig. 3 shows the ozone consumption levels in three of the six treatment systems utilizing ozone. The UVA irradiation (photolysis) in the presence of oxygen had no influence on the degradation of oxalic acid, while photocatalytic treatment showed a negligible effect: less than a 5% decrease in oxalic acid concentration after 100 min. Krysa et al. [8] proposed the mechanism of photocatalytic degradation of oxalic acid as below:

$$TiO_2(e^- + h^+) + O_2 + H_2O \rightarrow {}^\bullet O_2{}^- + {}^\bullet OH \quad (1)$$

$$HOOC\text{-}COO^- + {}^\bullet OH \rightarrow HOOC\text{-}COO^\bullet + OH^- \quad (2)$$

$$\text{And/or} \quad HOOC\text{-}COO^- + h^+ \rightarrow HOOC\text{-}COO^\bullet \quad (3)$$

$$HOOC\text{-}COO^\bullet \rightarrow H^+ + {}^\bullet CO_2{}^- + CO_2 \quad (4)$$

$$^\bullet CO_2{}^- + O_2 \rightarrow CO_2 + {}^\bullet O_2 \quad (5)$$

$$^\bullet O_2{}^- + H^+ \rightarrow HO_2{}^\bullet \quad (6)$$

Table 2
Abbreviations used in this paper.

C	Oxalic acid concentration
C_0	Initial oxalic acid concentration
TOC	Total organic carbon
TOC_0	Initial total organic carbon
PAG	Pilkington Active glass
BSG	Borosilicate glass
UVA	Near UV-light

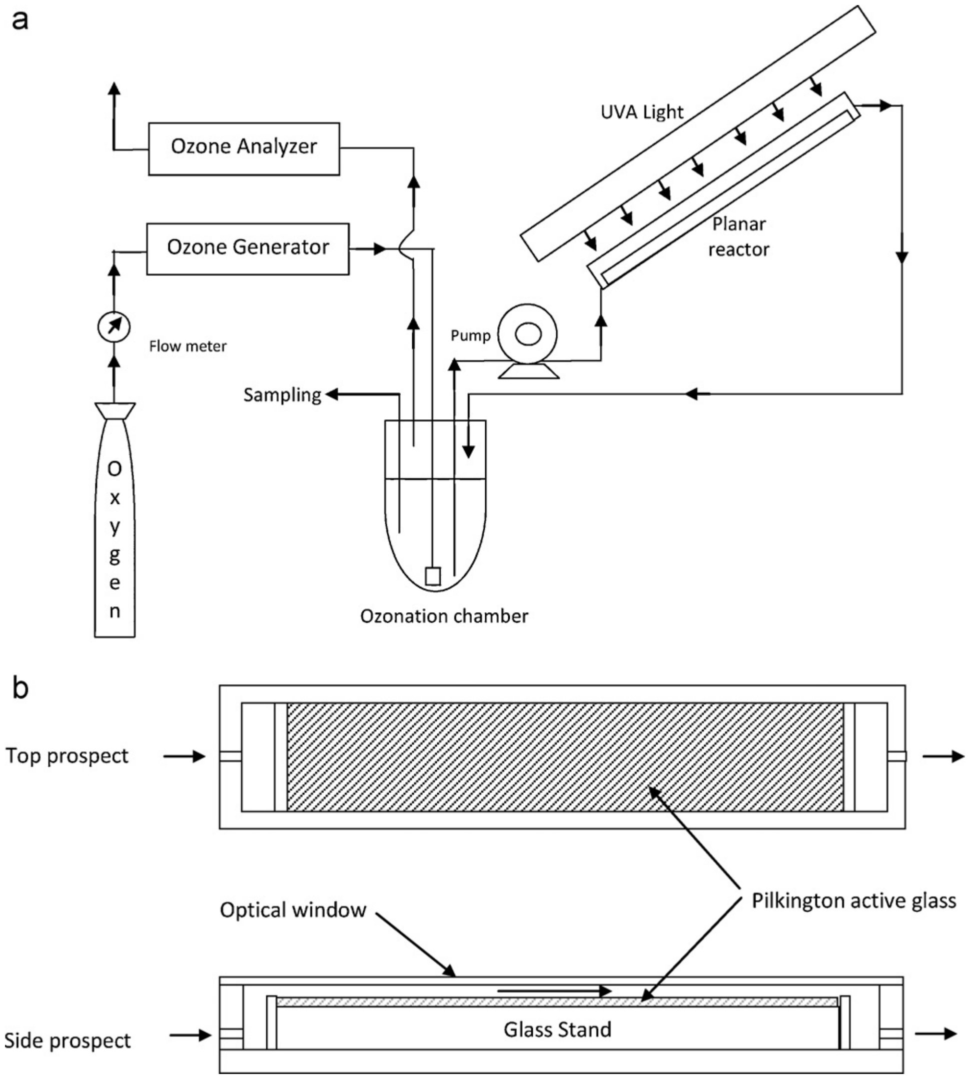

Fig. 1. (a) Setup details and (b) planar reactor's structure.

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \quad (7)$$

$$H_2O_2 + HO_2^{\bullet} \rightarrow {}^{\bullet}OH + H_2O + O_2 \quad (8)$$

Likewise, the ozonation and catalytic ozonation treatments reduced the initial oxalic acid concentration by 9–12% after the same time period, indicating that no remarkable heterogeneous catalytic ozonation occurred on the semiconductor surface. Furthermore, since Hoigné and Bader [23] reported that at acidic pH values the direct reaction rate constant between the ozone and oxalic acid molecules is very low, it is reasonable to conclude that the small ozone effect observed here was because of hydroxyl radicals generated by ozone decomposition [2] (reactions (9)–(11)) and the oxidation of oxalic acid molecules by these more powerful oxidants (reaction (2)).

$$O_3 + H_2O \rightarrow 2HO^{\bullet} + O_2 \quad (9)$$

$$O_3 + HO^{\bullet} \rightarrow O_2 + HO_2^{\bullet} \leftrightarrows {}^{\bullet}O_2^{-} + H^{+} \quad (10)$$

$$O_3 + HO_2^{\bullet} \leftrightarrows 2O_2 + HO^{\bullet} \quad (11)$$

$$2HO_2^{\bullet} \rightarrow O_2 + H_2O_2 \quad (12)$$

In spite of the fact that Addamo et al. [22] reported no noticeable decrease in the concentration of oxalic acid by the presence of ozone and UV light together in the reactor medium when compared to that of ozone alone, our system showed an effective degradation of oxalic acid during the photo-ozonation treatment, indicating that UVA irradiation played a more significant role in our setup conditions. The effect of UVA could be attributed to the higher amount of hydroxyl radicals produced during direct reaction of ozone with hydrogen peroxide molecules (reaction (13)) [28].

$$O_3 + H_2O_2 \rightarrow OH^{\bullet} + HO_2^{\bullet} + O_2 \quad (13)$$

$$O_3 + H_2O + h\nu \rightarrow H_2O_2 + O_2 \quad (14)$$

Hydrogen peroxide molecules are generated as an intermediate in ozone decomposition chain reactions (reactions (9)–(12)) and by irradiation of ozone molecules (reaction (14)) [28]. Despite the negligible adsorption of radiations with $\lambda > 300$ by hydrogen peroxide, very slight generation of hydroxyl radicals is probably occurring by adsorption of the short wavelengths existing in the spectrum of UV-light source used in the present study.

The higher level of ozone consumption in photo-ozonation compared to ozonation alone (Fig. 3) is in agreement with the two above mentioned possibilities; however, the ozone photolysis seemed to be more effective due to the generation of two hydroxyl radicals by the decomposition of one ozone molecule, while three ozone molecules are required to produce two hydroxyl radicals via ozone attack on water molecules.

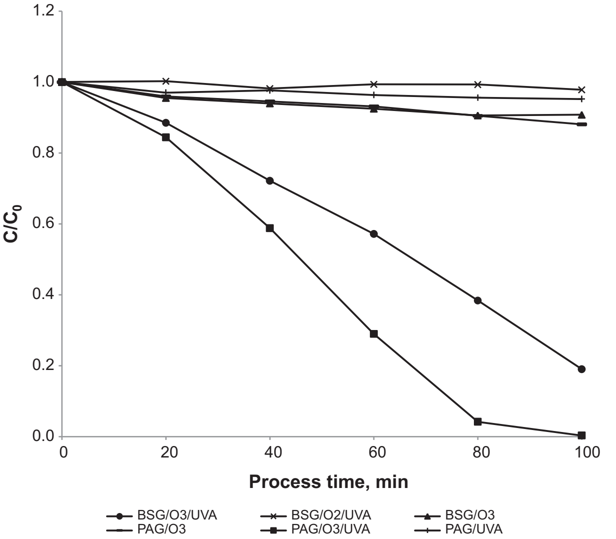

Fig. 2. Degradation of oxalic acid vs. time in 6 different oxidation systems, $C_0 = 10$ mM, T = 25 °C and pH = 2.1.

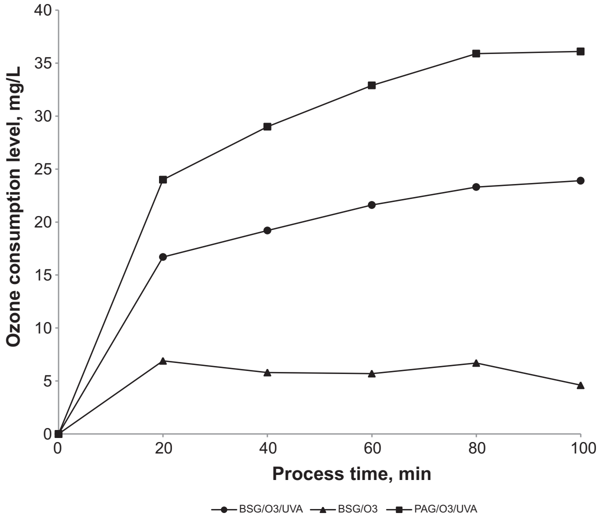

Fig. 3. Ozone consumption level vs. time in 3 different oxidation systems, $C_0 = 10$ mM, T = 25 °C and pH = 2.1.

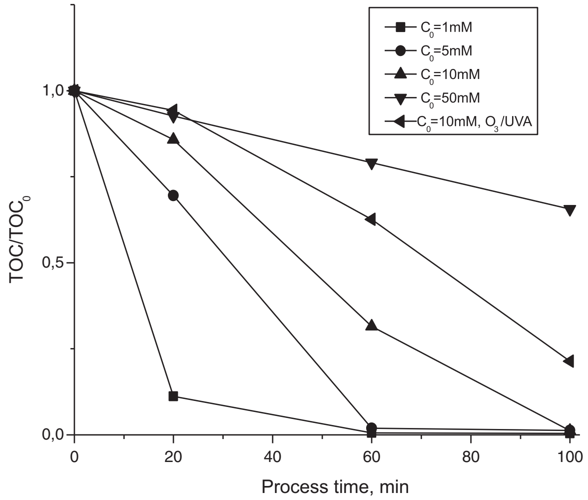

Fig. 4. TOC/TOC$_0$ level vs. time, T = 25 °C and pH = 2.1.

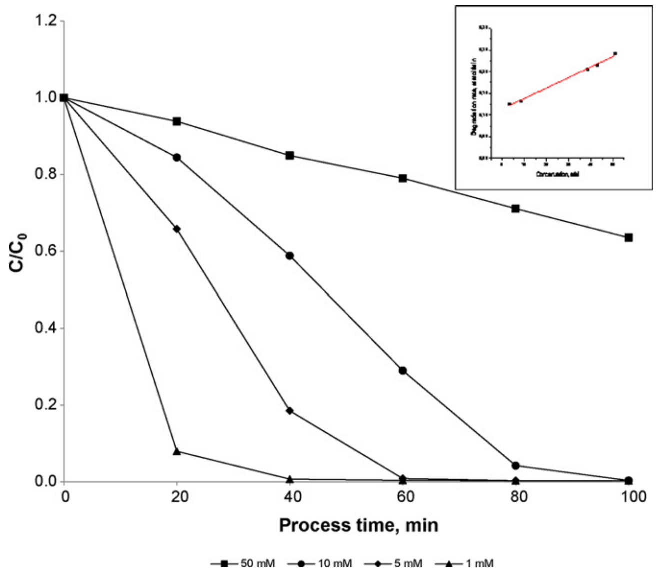

Fig. 5. Degradation of oxalic acid vs. time at different initial concentrations, T = 25 °C and pH = 2.1 (inset graph: degradation rate vs. concentration).

Fig. 4 shows that the mineralization of oxalic acid by O_3/UVA represents a similar trend to that found in the degradation of this compound.

Nevertheless, the highest degradation rate of oxalic acid and the highest level of ozone consumption occurred during photocatalytic ozonation, would indicate an enhancement of hydroxyl radical generation on the photocatalyst surface in addition to that brought by catalytic ozone decomposition in the TiO_2/ozone/UVA oxidation system. Considering that ozone reacts directly with the nucleophilic positions of organic compounds, and since oxalic acid molecules do not have such positions, a direct reaction between ozone and oxalic acid could be considered as negligible [29].

The influence of three significant practical variables (initial concentration of pollutant, solution pH value and temperature) on the degradation rate and ozone consumption level over the treatment time period was studied. It is worth noting that in such heterogeneous systems, where various simultaneous events happen, such as electron–hole pair generation on the irradiated semiconductor surface, their transfer and reaction with adsorbed molecules (ozone and/or oxalic acid) or further recombination with each other, diffusion of oxalic acid and ozone molecules into solution and their adsorption on the photocatalyst surface, ozone decomposition by irradiation, the direct attack of ozone on oxalic acid in the bulk of the solution or on the photocatalyst surface, formation of hydroxyl radicals as stronger oxidants for attacking the pollutants indirectly; to present a comprehensive and precise description of the involved mechanisms is a complicated task that is out of the scope of the present work.

3.1. Effect of the initial concentration of oxalic acid

The decomposition rate of oxalic acid was strongly affected by its initial concentration in our heterogeneous oxidation system. As expected, Fig. 5 shows that complete oxalic acid degradation was achievable in a shorter time for lower initial concentrations; nevertheless, a surprising result was observed where the biggest average degradation rate over the first 20 min was found at the highest initial concentration (Table 3), indicating that the oxidation capacity of our system was still open for the treatment of higher concentrations; however, the typical oxalic acid concentration in Bayer liquor varies between 10^{-5} M and 10^{-2} M [16,31]. Moreover, after reaching ozone saturation conditions (supposed to be after 20 min

Table 3
Initial degradation rate at different conditions.

Initial concentration (mM)	pH	Temperature (°C)	Average degradation rate over the first 20 min (mM/min)
1	2.1	25	0.047
5	2.1	25	0.088
10	2.1	25	0.081
50	2.1	25	0.167
10	3	25	0.225
10	5	25	0.075
10	7	25	0.066
10	9	25	0.048
10	2.1	10	0.046
10	2.1	40	0.138
10	2.1	55	0.213
10	2.1	70	0.124

from the treatment start point) the degradation rate for concentrations higher than 3 mM represented a linear trend vs. concentration (Fig. 5, inset graph). In addition, Fig. 4 shows the initial concentration effect on total mineralization of oxalic acid. It is evident that in our setup conditions, solutions of 5 mM oxalic acid were mineralizable after 1 h treatment, as rapid as the degradation in the same period of time.

Fig. 6 illustrates an evident decrease in the ozone consumption after 40 min and 60 min for concentrations of 1 mM and 5 mM, respectively, where no more oxalic acid was detectable according to Fig. 5 for each one of these two conditions. At the same time, a remarkable increase in the ozone consumption over the time period was observed in the case of 50 mM which matches the results mentioned above.

3.2. *Influence of solution pH*

Despite being a carboxylic acid, oxalic acid is categorized among some relatively powerful acids.

$$C_2O_4H_2 \leftrightarrows C_2O_4H^- + H^+, \quad pK_{a1} = 1.27 \qquad (15)$$

$$C_2O_4H^- \leftrightarrows C_2O_4{}^{2-} + H^+, \quad pK_{a2} = 4.28 \qquad (16)$$

The pH value appoints the predominant existing chemical species present in an aqueous solution of a relatively strong dicarboxylic acid. In our case, the oxalic acid could be present as a neutral molecule, as hydrogen oxalate anion or as oxalate anion. On the other hand, the adsorption rate of oxalic acid molecules on the photocatalyst surface and the consequent degradation of this compound by hydroxyl radicals are highly dependent on the interactions between the existing forms of these molecules in solution and the surface groups on the photocatalyst. In the present study conditions the oxalic acid was mainly comprised of $C_2O_4H^-$, 87–98% between pH 2.1 and pH 3, although $C_2O_4{}^{2-}$ was the main form of oxalic acid in the solution at pH >5 (84%). Fig. 7 depicts the influence of solution pH on the degradation of oxalic acid. As far as the adsorption levels of oxalate and hydrogen oxalate at the photocatalyst surface are concerned, oxalic acid degradation trends were definitely different for the two pH ranges mentioned above, pH >4 and pH <4. Total removal of oxalic acid was achievable at the end of the process time at pH 2.1, and the degradation was almost 2 and 2.5 times higher at pH 3 compared to pH 5–7 and pH 9, respectively. However, treatment at pH 3 showed unexpected results by revealing a sharp decrease in the concentration during the first 20 min and continued with a slight slope. Furthermore, ozone consumption levels during the treatment at pH 3 determined an anomalous developing at the same time, Fig. 8. This behaviour could be attributed to the coupling of catalytic ozone decomposition and the generation of hydroxyl radicals beside effective hydroxyl radical generation from the non-catalytic ozone decomposition at pH 3, which was limited at more acidic pH values [2]. The next slight slope at these conditions (pH 3) agreed with our assumption that non-catalytic hydroxyl radical generation is stopped by when more acidic conditions are reached during the oxidation process. Hermann et al. [30] also reported a similar maximum performance in the oxidation of oxalic acid at pH 2.34 during a photocatalytic process in an aqueous suspension.

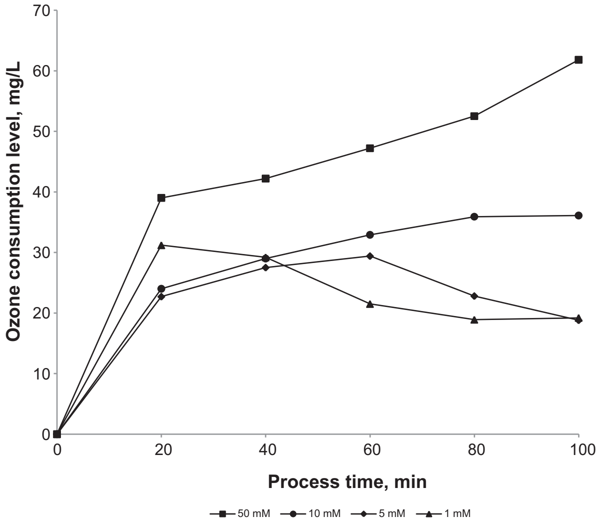

Fig. 6. Ozone consumption level vs. time at different initial concentrations of oxalic acid, T = 25 °C and pH = 2.1.

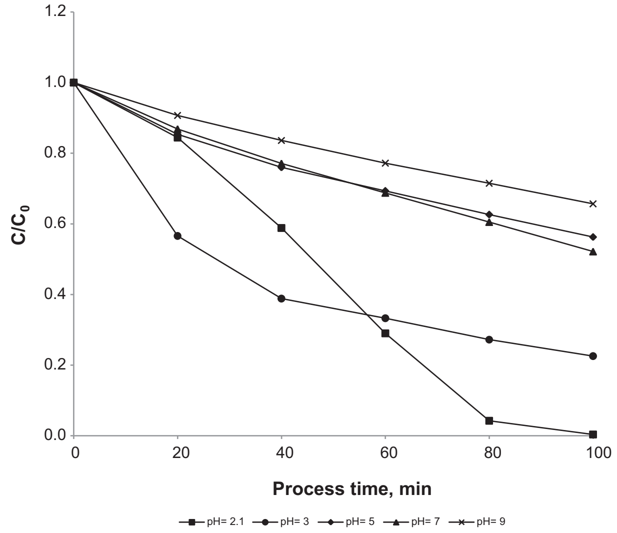

Fig. 7. Degradation of oxalic acid vs. time at different pH values, C_0 = 10 mM and T = 25 °C.

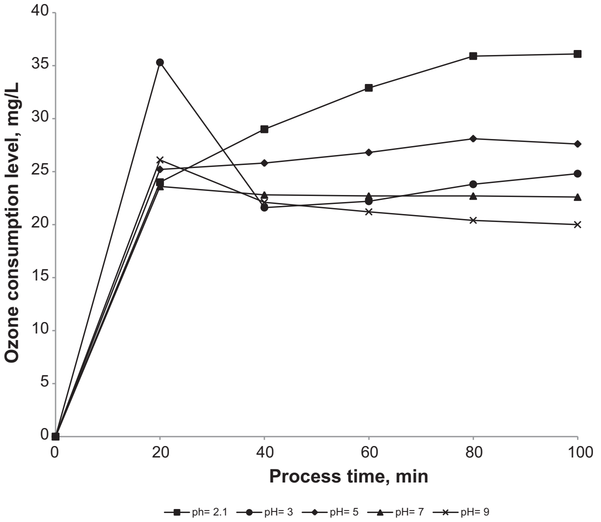

Fig. 8. Ozone consumption level vs. time at different pH values, $C_0 = 10$ mM and T = 25 °C.

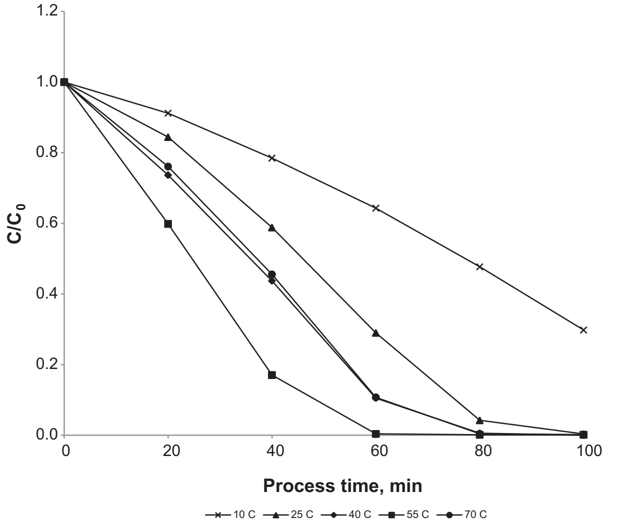

Fig. 10. Degradation of oxalic acid vs. time at different temperatures, $C_0 = 10$ mM and pH = 2.1.

Fig. 9 illustrates the influence of pH on the mineralization of oxalic acid. According to Figs. 7 and 8, the decreased oxalic acid degradation rate and contemporary lower ozone consumption level at pH ≥ 5 is explained by the weaker adsorption of $C_2O_4^{2-}$, which is the main form of oxalic acid on the photocatalyst surface at this pH range, accompanied by the decreased catalytic ozone decomposition. However, it is proposed that the generation of hydroxyl radicals from non-catalytic ozone decomposition is likely to be the main pathway for promoting the oxidation process under these conditions.

3.3. Temperature effect

According to Fig. 10, an increase in the temperature from 10 °C to 55 °C increased the degradation rate of oxalic acid, while even higher temperatures of up to 70 °C had a negative effect and reduced the degradation rate to that observed at 40 °C, approximately. Temperature variations influence heterogeneous oxidation systems in several ways which are usually considered as being opposite to each other and act either to develop or to inhibit the treatment. In other words, the observed influence of temperature is a consequence of many co-current and/or counter-current functions. On one hand, according to the Freundlich adsorption isotherm, $x/m = kP^{1/n}$ where x, m, P are the quantity adsorbed, the mass of the adsorbent and the pressure (or concentration), respectively, and k and n are empirical constants for each adsorbent–adsorbate pair at a given temperature, as the temperature increases at a constant pressure (or concentration) the adsorption rate is negatively induced and the quantity adsorbed raises more slowly, leading, as a result, to a decrease in the degradation of adsorbed particles on the photocatalyst surface. Furthermore, an increase in temperature decreases ozone solubility in water, so that negligible ozone solubility in water under conventional conditions is reported above 43 °C. This effect causes a shortage in the ozone molecules available to handle the photocatalytic ozonation process, and this is possibly the main factor hindering the efficiency of the process at higher temperatures. On the other hand, any temperature increase should result in higher rates for all chemical reactions involved in such heterogeneous treatments. The unexpected increasing trend of the oxalic acid degradation rate between 40 °C and 55 °C could be explained by the high ozone content in the input oxygen–ozone mixture gas (ca. %10 .wt) and the accelerated rate of ozone decomposition producing hydroxyl radicals under these conditions.

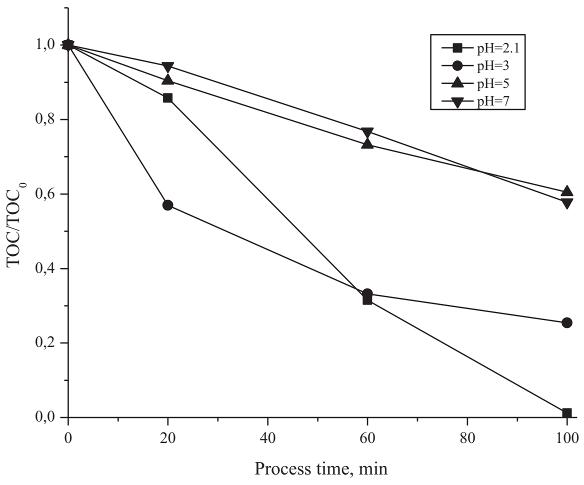

Fig. 9. TOC/TOC$_0$ level vs. time at different pH values, $C_0 = 10$ mM and T = 25 °C.

It is worth noting that since the oxalic acid photocatalytic oxidation with $E_a = 45.8$ kJ/mol and the consequent transfer of photogenerated holes and electrons to the adsorbed particles on the photocatalyst surface are categorized as low activation energy processes [31], this factor does not seem to be vital in promoting oxalic acid photocatalytic ozonation by shifting to higher temperatures.

In Fig. 11 it is evident that increased temperatures of up to 55 °C enhanced the rate of oxalic acid decomposition and also increased the ozone consumption in our heterogeneous system. As temperatures were higher than 40 °C, the oxalic acid content was almost completely degraded after approximately 60 min (Fig. 10), leading to a significant reduction of ozone consumption during the last 40 min of oxidation.

Just like for the oxalic acid initial concentration and for the solution pH, Fig. 12 shows that the effect of solution temperature on the mineralization rate of oxalic acid was similar to the effect observed for the degradation rate of this compound, which emphasizes the fact that oxalic acid degradation leads to direct mineralization without the production of stable intermediates.

Considering the Arrhenius plot given in Fig. 13, the activation energy related to the degradation of oxalic acid in our heterogeneous photocatalytic ozonation system was about 26.5 kJ/mol.

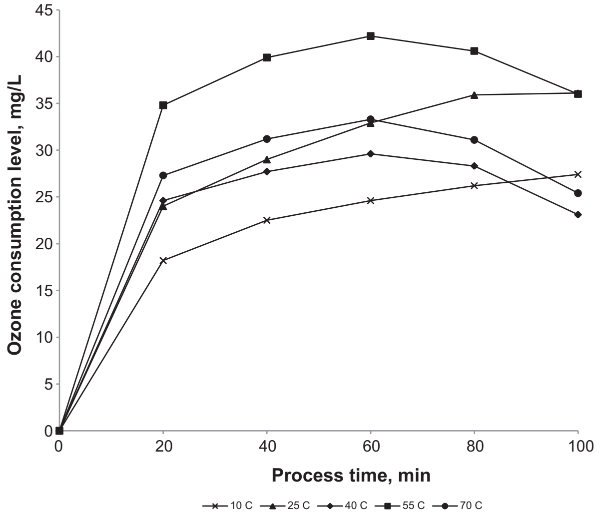

Fig. 11. Ozone consumption level vs. time at different temperatures, $C_0 = 10$ mM and pH = 2.1.

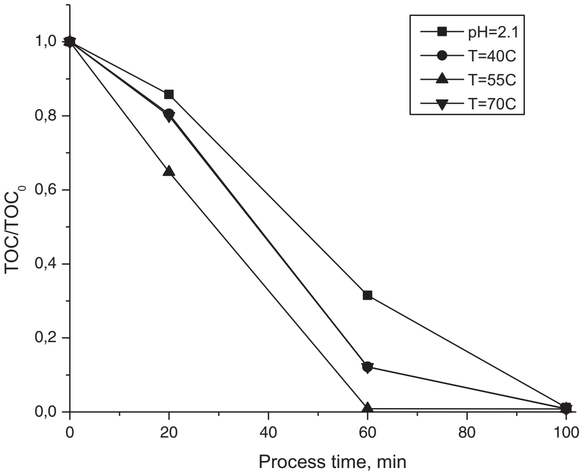

Fig. 12. TOC/TOC$_0$ level vs. time at different temperatures, $C_0 = 10$ mM and pH = 2.1.

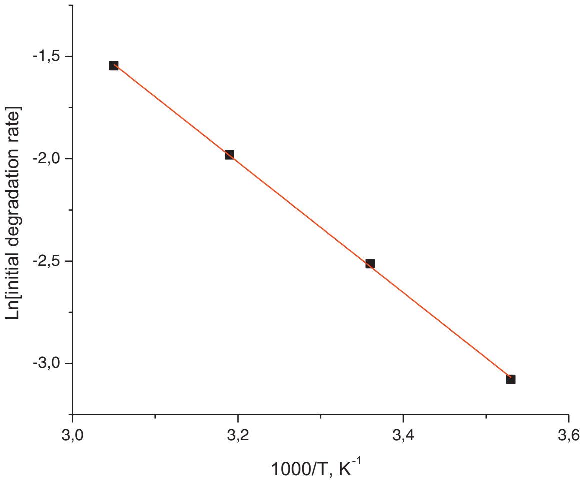

Fig. 13. Arrhenius plot, $C_0 = 10$ mM and pH = 2.1.

4. Conclusions

The Pilkington Active^{TM} glass as a commercial product accompanied by ozone and UV light effectively removes oxalic acid molecule pollution in water. The obtained results show that under present experimental conditions, the lower the initial oxalic acid concentrations, the shorter the degradation time periods in such heterogeneous photocatalytic ozonation treatments. However, the highest investigated initial concentration gave the best average degradation rate over the first 20 min. Furthermore, increased temperatures of up to 55 °C have raised the degradation rate and the ozone consumption level, whereas temperatures higher than 55 °C caused a negative influence. Acidic pH conditions increased the treatment performance since pH 2.1 caused a total disappearance of oxalic acid after 100 min and the most noticeable average degradation rate over the first 20 min was found at pH 3. The TOC results in our study agree with the fact that oxidation of oxalic acid to CO_2 and H_2O is directly attainable without any formation of stable intermediate products.

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