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Comparative photocatalytic degradation using natural and artificial UV-light of 4-chlorophenol as a representative compound in refinery wastewater

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Abstract

The comparison of the degradation of 4-chlorophenol, using sunlight and a UV-lamp, was carried out using two different catalysts, Degussa P25 and Hombikat UV 100. All experiments were performed after first optimizing the catalyst concentrations and pH. The optimal concentrations for Degussa P25 and Hombikat UV 100 occurred at 7 and 10 g/l, respectively. The optimal initial pH was found to be 5 for both catalysts. The degradation rate of 4-chlorophenol is 6.4 times and 1.6 times higher when using sunlight compared to the artificial UV-lamp for Degussa P25 and Hombikat UV 100, respectively. The degradation rate of 4-chlorophenol is six times higher, compared to Hombikat UV 100, at the optimal conditions, when using sunlight and Degussa P25 as the catalyst. The chloride produced during the reaction was measured and found to be highest for Degussa P25 with sunlight as the energy source.

Keywords: 4-Chlorophenol; Titanium dioxide; Sunlight; Photocatalyst

1. Introduction

Organic contaminants present in industrial wastewater are of major concern with respect to the health of the general public. There are several established ways for the removal of such contaminants. The most widely used of these methods is biological treatment. Other important applied methods include adsorption on activated carbon, hydrogen peroxide/UV-light, Ozone/UV/hydrogen peroxide and γ-radiolysis [1–4]. In recent years, much attention has been paid to “photocatalytic detoxification” as an alternative technique, where the pollutants are degraded by UV-irradiation of a semiconductor suspension such as titanium dioxide or zinc oxide [5–9]. Photocatalysis with titanium dioxide is based on the formation of pairs of electron/positive holes (e^-/h^+), when the photocatalyst is subjected to UV-light [10]. The electron holes may induce reduction, but in most cases, in the presence of oxygen, they lead to the formation of superoxide anions [11]. Positive holes oxidize adsorbed organic substrates or react with water leading to the formation of hydroxyl radicals, which are very efficient oxidizing agents (the oxidation potential of OH radicals is as high as 2.80 V). The hydroxyl radicals produced are very reactive, and react rapidly and non-selectively with organic compounds leading to, in the last step of the reaction, the total mineralization of the organic substrate [12].

The photocatalytic oxidation of chlorophenols in aqueous solution has received considerable attention because these compounds are important xenobiotic micropollutants of the aquatic environment, originating from different branches of the chemical industry [13–18]. Several studies have been published in the literature dealing with the degradation of chlorophenol compounds using different catalysts under different conditions [19–26].

To our knowledge, there is no direct comparison in the literature of 4-chlorophenol degradation using an artificial and a natural UV-lamp. In this paper, we have studied the degradation rate of 4-chlorophenol using two different catalyst types at different conditions, using both natural sunlight and artificial UV-light. It is one of the first steps in our systematic studies of Ras Lanuf Oil and Gas Processing Co. (RASCO) wastewater in order to optimize and apply this technology in the actual effluent treatment plant.

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2. Materials and methods

2.1. Reagents and instruments

4-Chlorophenol was purchased from Seelze-Hannover and purified before use. TiO_2 (Degussa P25, particle size 20–30 nm, BET surface area 50–15 m^2/g, 70% anatase and 30% rutile) was obtained from Degussa GmbH. TiO_2 Hombikat UV 100 (primary particle size, 10 nm, BHT surface area >250 m^2/g, >99% anatase) was purchased from Sachtleben Chemie GmbH. The water used in the experiments was distilled and demineralised by the Ras Lanuf Oil and Gas Processing Co. utility plant. The nitrogen gas used was obtained from the RASCO nitrogen plant with 99.99% purity. The oxygen gas was obtained from B.O.C. Ltd. with 99.999% purity, grade N 4.8. HPLC grade acetic acid and acetonitrile were obtained from Sigma–Aldrich. Potassium biphthalate, orthophosphoric acid and anhydrous bicarbonate, were obtained from BDH.

The TOC instrument used in this project was manufactured by Skalar-company, Holland, and is equipped with an IT-detector, a TC-reactor with a maximum temperature of 950 °C, an IC-reactor and an autosampler. The injection volume used was 100 μl and the oven temperature was adjusted to 680 °C. A 3071 Jenway type pH-meter was used for pH measurements. The samples were centrifuged using Seta-IEC from Stan-Hop-Seta. The light intensity was measured using a UVA-meter from Dr. Hoenle GmbH. The UV-lamp used in the degradation experiments was manufactured by Philips, M44GS-100/M, 100 W mercuric lamp. The HPLC experiments were carried out on a CECIL machine manufactured by CECIL, UK. The instrument is equipped with a CE2020 UV-detector CE1100 pump. A spherisorb 80A column was used with a 25 cm length and 4.6 mm inner diameter. A combination of acetic acid:water:acetonitrile 1:55:44 was used as the eluent. The flow rate was 1 ml/min and the injection volume was 20 μl. The UV-measurements were performed on a PYE UNICAM PU 8600 UV-Vis spectrometer, manufactured by Philips.

3. Experimental

3.1. Preparation of 4-chlorophenol stock solutions

A 1.785 g (0.01388 mol) of 4-chlorophenol were dissolved in 1 l of distilled and demineralized water in order to prepare 1000 ppm carbon as a stock solution. A 100 or 25 ml from the stock solution were transferred using a pipette into 900 or 225 ml of water, respectively, to yield 100 ppm TOC and 178.5 ppm 4-chlorophenol.

3.2. Procedure for the photodegradation experiments

The photoreactor consisted of a 3 l beaker made of Pyrex-glass, with a 17 cm inner diameter and a 7 cm height, equipped with a magnetic stirring bar and an oxygen-purging device which consisted of two gas washing bottles and two sintered glasses. One bottle was filled with pure water to humidify the oxygen and to minimize evaporation of water in the beaker. One liter of 100 ppm TOC (178.5 ppm 4-chlorophenol) and the required amount of the photocatalyst were poured into the reactor and the initial pH was adjusted to the desired values. The suspension was stirred under continuous bubbling of oxygen for at least 1 h inside the laboratory to reach a state of system equilibrium. The reactor was then exposed to sunlight and the suspension was irradiated for 8 h.

Fifteen milliliters of the sample were taken before the addition of the photocatalyst and directly before exposing the system to the sun. Fifteen milliliters of the sample were then taken at regular intervals (every 60 min) during irradiation. These samples were not returned to the bulk solution. Consequently, there was a decrease in volume during the experiment. However, the number of analyses done and volume needed on a given run was limited so that the volume decrease in the illuminated solution was less than 15%.

The pH was measured immediately before the samples were taken and the TOC and compound concentration were determined after centrifuging the suspension for 15 min at 1500 rpm according to standard ASTM D1252 methods (ASTM, 1993). The UV-intensity was determined at regular intervals using a UV-meter (Dr. Hoenle UVA-meter). The same procedure was followed when using the UV-lamp as the energy source.

3.3. TOC experiments

A 2.1254 g (0.0104 mol) anhydrous potassium biphthalate was dissolved in 1 l of demineralized water to make a 1000 ppm carbon stock solution. The pH of the solution was adjusted to 2 using orthophosphoric acid. A series of concentrations (20, 40, 60, 80, and 100 ppm) were prepared and injected into the instrument in order to generate the TC calibration curve. For the inorganic carbon (IC) calibration curve, 4.4122 g (0.053 mol) anhydrous sodium carbonate and 3.4970 g (0.0416 mol) anhydrous sodium bicarbonate were dissolved in 1 l of demineralized water to yield 1000 ppm inorganic carbon. Different concentrations were prepared (20, 40, 60, 80, and 100 ppm) for the IC calibration curve.

The TOC is the difference between TC and IC:

$$\mathrm{TOC} = \mathrm{TC} - \mathrm{IC}$$

where TOC is the organic carbon that is converted into carbon dioxide after oxidation; TC the total carbon in a sample. This includes organic, inorganic, and volatile TC. It is represented as the total mass of carbon per amount of sample. IC is the inorganic carbon in a sample that, after acidification, turns into carbon dioxide.

Prior to sample injection into the TOC, 10–15 ml were collected from the suspension. The solution was acidified to pH 2 and centrifuged for 15 min at 1500 rpm in order to separate the catalyst. Aliquots were gently purged with nitrogen before analysis to remove any dissolved carbon dioxide.

3.4. HPLC experiments

The HPLC instrument was calibrated using 4-chlorophenol standard solutions of 50, 100, 150 and 200 ppm. The concentration of the pollutants was measured at 254 nm. The samples injected into the HPLC were from the same solutions used for the TOC experiments.

3.5. Chloride experiments

3.5.1. Generation of the calibration curve

A 1.648 g (0.02820 mol) sodium chloride were dissolved in 1 l distilled and demineralized water to prepare 1000 ppm Cl^- as stock solution. A series of concentrations 0, 2, 4, 6, and 8 ppm chloride were prepared and the absorptions were read on the UV-spectrophotometer at 463 nm wavelength using a 2 cm cell. The calibration curve and sample analyses were performed as described in ASTM D2384-83 (re-approved 1994).

3.5.2. Sample analysis

An appropriate volume of sample was collected from the suspension. After the separation of the catalyst particles, 2–5 ml of the clear solution was diluted to 25 ml with demineralized water. Five milliliters of reagent 1, ammonium ferric sulfate (61.4 g $Fe(NH_4)_3SO_4$ + 200 ml H_2O + 283 ml conc. HNO_3, all diluted with water to 1 l) and 3 ml of reagent 2, saturated solution of mercuric thiocyanate (3 g $Hg(SCN)_2$ dissolved in methyl alcohol), were then added, and left for 10 min. The chloride content was read at 463 nm on the spectrophotometer using a 2 cm cell.

4. Results and discussion

The ultimate goal of all literature studies using titanium dioxide as a photocatalyst for organic pollutant destruction is to be able to apply this technology utilizing solar energy as the energy source. Accordingly, this work addresses the direct comparison of artificial and natural energy sources in order to apply this technique in the wastewater treatment plant of the RASCO refinery. The comparison experiments were carried out using two different catalyst types, Degussa P25 and Hombikat UV 100. Fig. 1 shows the degradation rate of 4-chlorophenol using sunlight at an average light intensity of 3.2 W/cm^2 and a UV-lamp at 3.2 W/cm^2, under optimal reaction conditions. From the results obtained, it is possible to conclude that the degradation rate of 4-chlorophenol is higher when using direct sunlight compared to the UV-lamp at the same light intensity. Increasing the light intensity of

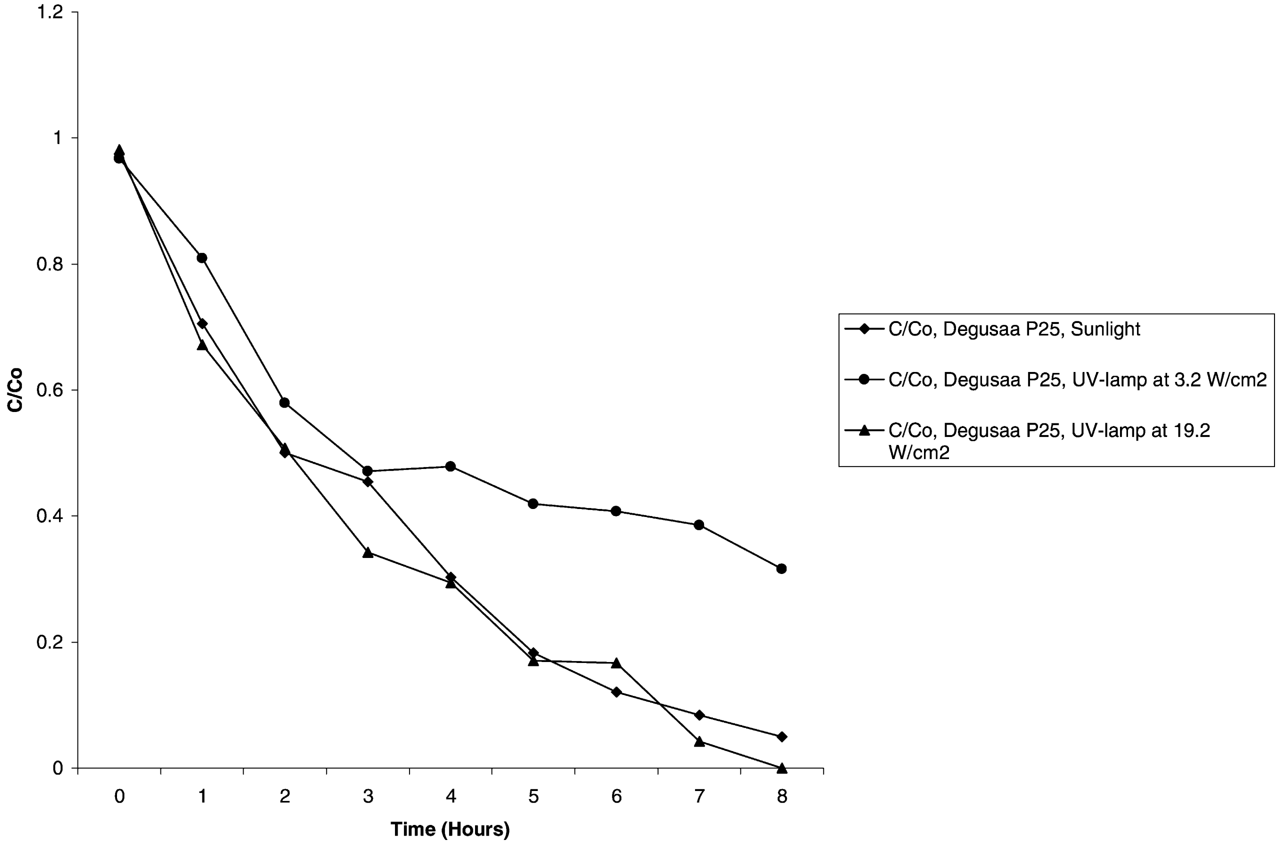

Fig. 1. Comparison of 4-chlorophenol degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 7 g/l Degussa P25.

the UV-lamp to 19.2 W/cm^2 produces only a slight improvement in the degradation process. Total organic carbon measurements performed on the same samples indicate that the complete mineralization of the pollutant was not achieved.

Taking our previous studies into consideration, it is interesting to note that the degradation rate of 4-chlorophenol is faster than phenol and slower than 1-naphthalene acetic acid [27]. The reason for this could be attributed to a combination of two factors, the adsorption/desorption-effect, and the reaction of the produced hydroquinone/benzoquinone intermediates with the electron/hole of the catalyst. It is known in the literature that such compounds have the ability to equilibrate with each other using the electron/hole of the catalyst [25]. In other words, such intermediates are able to short circuit the photocatalyst and negatively affect the photonic efficiency of the catalyst.

Repeating the same experiments using the other type of photocatalyst, Hombikat UV 100 at the optimized pH level and catalyst concentration, revealed that the degradation rate of 4-chlorophenol, using sunlight at the average light intensity of 3.2 W/cm^2, is 1.6 times higher than when using the UV-lamp at the same light intensity. In addition, the degradation rate is 1.4 times higher than when using the UV-lamp at 19.2 W/cm^2. The TOC results of the same sample show the same trend. Of course, here as always, total mineralization was not attained.

Comparing the results in Figs. 1 and 2 with 3 and 4, one is able to conclude that the degradation rate is six times higher when using Degussa P25 than when using Hombikat UV 100.

The total mineralizaion of 4-chlorophenol leads to the production of carbon dioxide, water, and hydrochloric acid, according to the following equation:

$$2C_6H_4OHCl + 13O_2 \xrightarrow{TiO_2,h\nu} 12CO_2 + 4H_2O + 2HCl$$

The effect of chloride ions on the degradation rates of the pollutants in aqueous solution is discussed in detail in the literature, and is believed to be quite negative. There are three different issues addressed:

- At low pH levels (<5), the catalyst exists primarily as $TiOH^+$ and TiOH. Under these conditions, the negatively charged chloride ions are attracted to the catalyst surface therefore competing with pollutant species for active sites, resulting in low degradation rates [20].
- The chloride ions in the suspension could act as electron scavengers competing, in this case, with molecular oxygen. This will inhibit the formation of the superoxide radicals that are essential for the formation of the actual oxidation agent, the hydroxyl radicals. The efficiency of the photocatalyst would once again be decreased [28,29].
- Another possible reaction of the chloride ions could be with the free radicals in the suspension, leading to the consumption of the radicals that are desired in high concentration in order to react with organic pollutants [30].

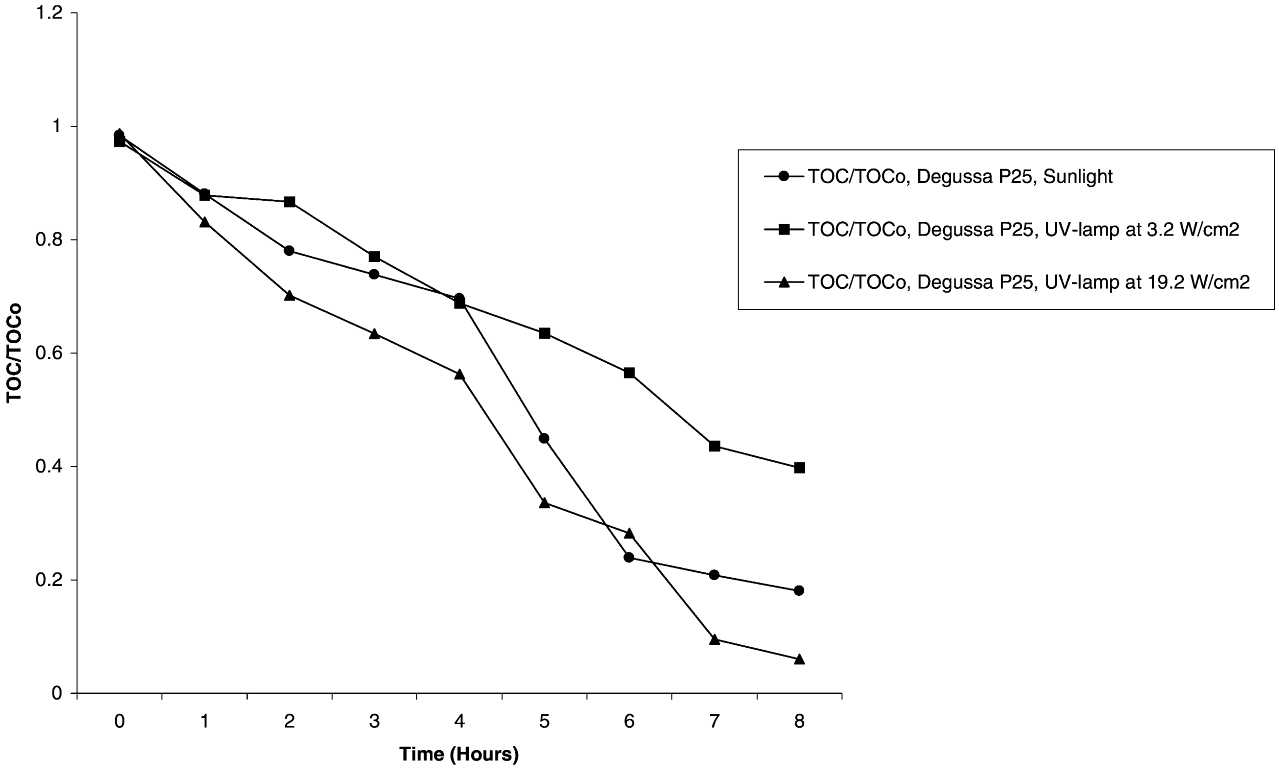

Fig. 2. The TOC comparison of 4-chlorophenol degradation at pH 4 and catalyst concentration 7 g/l Degussa P25.

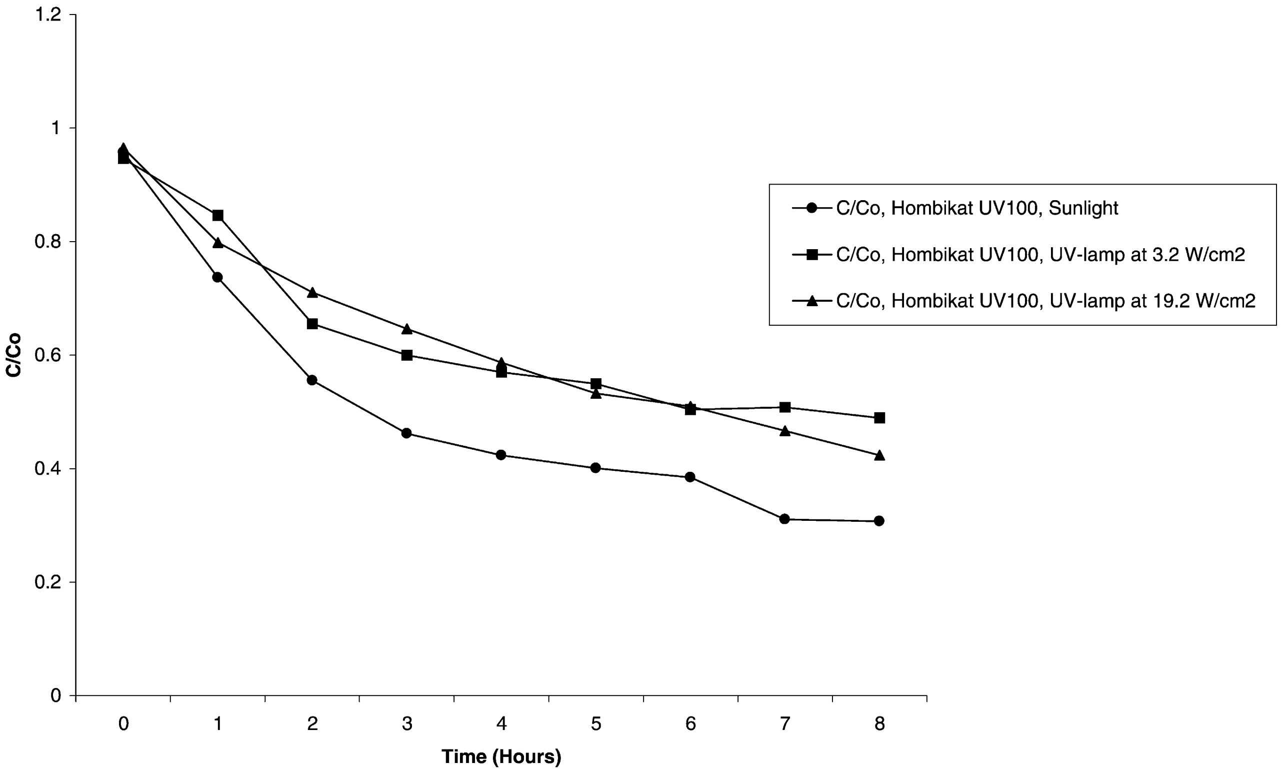

Fig. 3. Comparison of 4-chlorophenol degradation using sunlight and UV-lamp at pH 5 and catalyst concentration 10 g/l Hombikat UV 100.

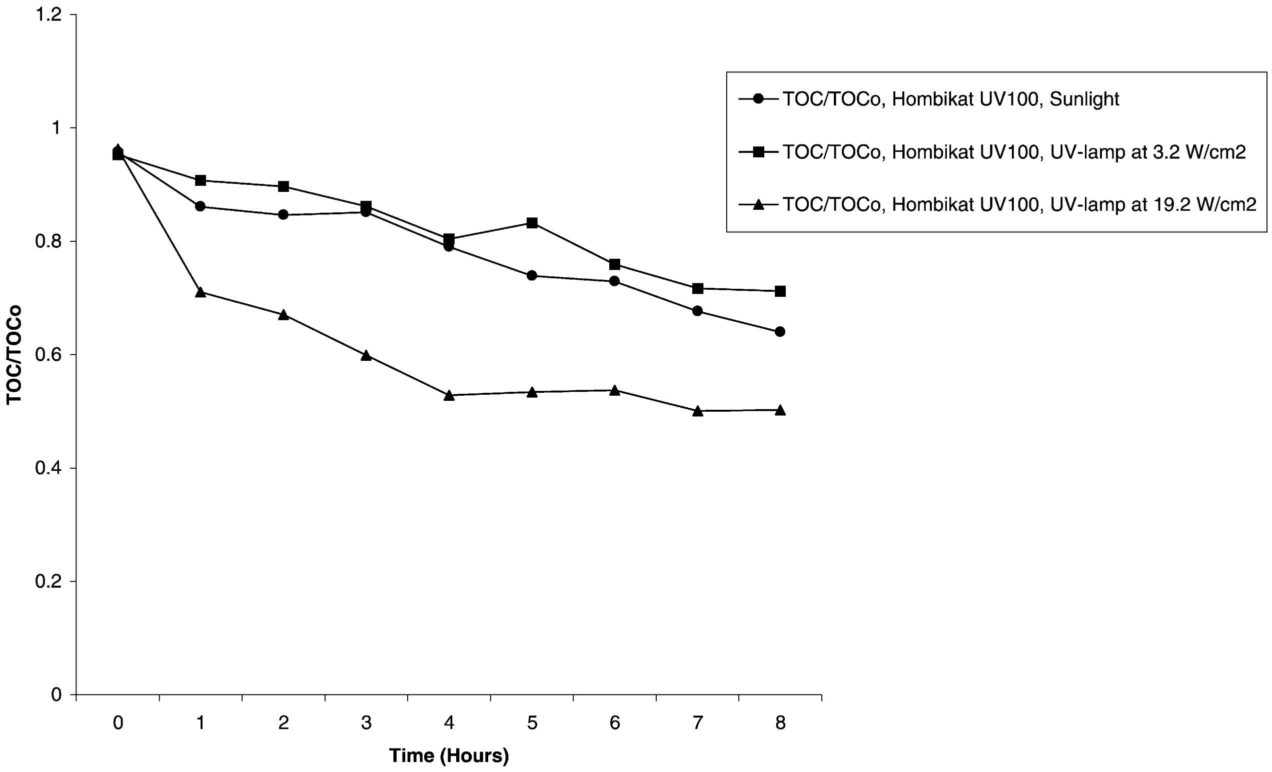

Fig. 4. The TOC comparison of 4-chlorophenol degradation at pH 4 and catalyst concentration 10 g/l Hombikat UV 100.

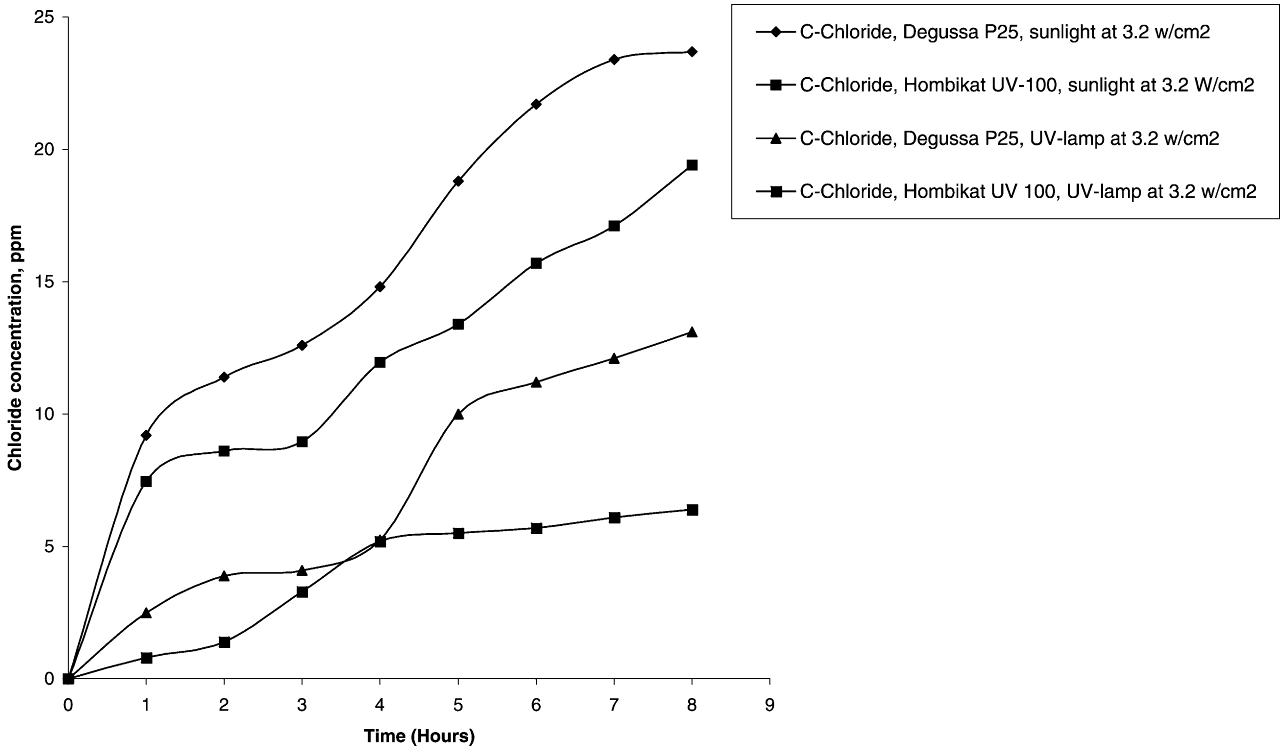

Fig. 5. Comparison of chloride concentration increase during the degradation of 4-chlorophenol using sunlight and UV-lamp for Degussa P25 (7 g/l) and Hombikat UV 100 (10 g/l).

Due to the above-mentioned side effects of the chloride ions, we decided to follow chloride formation during the reaction and to study its effect on the degradation rate of the pollutant, 4-chlorophenol. Moreover, this experiment was necessitated due to the presence of chloride in RASCO wastewater, originating from other sources in the refinery that could affect the degradation rate of the pollutants when putting this technology into place in the plant. Fig. 5 shows that the formation of chloride ions is more rapid when using Degussa P25 as the catalyst, rather than Hombikat UV 100. Our experiments indicate that the liberation of chloride ions does not seem to have a significant effect on the degradation process. The highest chloride concentration was obtained when using Degussa P25 and sunlight, while at the same time exhibiting the highest degradation.

5. Conclusion

The photocatalytic degradation of 4-chlorophenol was found to be optimal when using direct sunlight at the average light intensity of 3.2 W/cm^2, versus the artificial UV-lamp at the same light intensity. The degradation rate of 4-chlorophenol is six times higher when using Degussa P25 compared to Hombikat UV 100. The chloride ions liberated during the degradation process do not have a significant effect on the degradation process at the given initial pH of 5.

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