Heterogeneous and homogeneous photoassisted wastewater treatment

G RUPPERT*¹, K HOFSTADLER¹, R BAUER¹ and G HEISLER²

¹Institute of Physical Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Wien, Austria

²Austrian Energy and Environment, SGP/Waagner-Biró GmbH, Siemensstr. 89, A-1210 Wien, Austria

Abstract. Photochemical degradation of 4-chlorophenol (4-CP) as a model wastewater contaminant with three methods: UV/TiO₂, UV/H₂O₂ and UV/TiO₂/H₂O₂ ($\lambda > 310$ nm) has been investigated and compared to the dark Fenton reaction and to direct photolysis. A UV-irradiated combination of TiO₂ and H₂O₂ was found to be the most effective degradation method for TOC (total organic carbon). 4-CP was degraded most rapidly by the dark Fenton reaction. In the heterogeneous process on illuminated TiO₂ without H₂O₂, only small amounts of by-products were formed during irradiation in contrast to homogeneous processes where H₂O₂ was involved. During UV/H₂O₂ and Fenton experiments, coloured by-products appeared during irradiation and degradation rates of 4-CP and TOC showed strong differences between homogeneous and heterogeneous processes.

Keywords. Wastewater treatment; photooxidation; hydroxyl radicals; titanium dioxide; Fenton reaction.

1. Introduction

Chemical oxidation of organic contaminants in wastewater is an effective method to remove pollutants without further environmental problems. In contrast to other wastewater treatment methods, e.g. adsorption on activated granular carbon or air stripping, the contaminants are converted to harmless materials such as carbon dioxide and inorganic salts. Various processes suggested for oxidation of organic compounds are UV-photolysis in the presence of H₂O₂ [(1)] or ozone, photolysis on UV-irradiated TiO₂, (3) + (4), and on the system Fe²⁺/H₂O₂ (Fenton reaction, (2)). The active species in all photochemical processes is the hydroxyl radical (Haag and Yao 1992), a strong oxidant with an oxidation potential of 2.8 V. It is generated, e.g., by the following reactions (Carey 1990):

(a) homogeneous

or

(b) heterogeneous

---

*For correspondence

In this work, the degradation of 4-chlorophenol (4-CP, 1.01×10^{-3} mol/l = 72.9 ppm TOC) and of TOC (total organic carbon) by photochemical methods with UV/H₂O₂, UV/TiO₂, and UV/TiO₂/H₂O₂, has been studied. The results were compared to the dark Fenton reaction, and to photolysis without additives.

Chlorophenols are widely used in the manufacture of herbicides and fungicides. Their traces were found in ground water but also in drinking water (caused by the disinfection of phenolic waters with chlorine). Because of their low biodegradability, chemical methods for the removal of chlorophenols have been developed. Degradation of chlorophenols (with low substrate concentrations) using UV-photolysis (Yasuhara *et al* 1977), UV-illuminated TiO₂ (Matthews 1987), UV-photolysis with H₂O₂-addition (Moza *et al* 1988) and Fenton's reagent (Barbeni *et al* 1987) was reported elsewhere.

2. Experimental details

4-Chlorophenol (4-CP, reagent grade, Merck), TiO₂ (Degussa P25), H₂O₂ (30%, p.a., Riedel de-Haën) and FeSO₄·7H₂O (p.a., Merck) were used without further purification.

All experiments were performed at an initial pH of 5.8 in a three-necked-2l flask equipped with a plane glass window (Duran, irradiated area 3300 mm²) and thermostatted at 25°C. The initial concentration of 4-CP was 1.01×10^{-3} mol/l (= 72.9 ppm TOC). A 400 W high pressure Hg-lamp (Osram Ultramed) with quartz optics and water filter was used as light source. The solution (2000 ml) was stirred and purged with pure oxygen during the reaction. Concentration of TiO₂-suspension was 2 g/l, molar excess of H₂O₂ was 10:1 or 50:1 in comparison to 4-CP, concentration of Fe²⁺ in the Fenton experiment 2.5×10^{-4} mol/l. 4-CP was analysed by HPLC (column: Spherisorb S5 ODS 50 µm, eluent: methanol:H₂O = 40:60 Vol%, flow: 1 ml/min), TOC was monitored with a TOC analyser (Shimadzu). H₂O₂ was determined by a modified iodometric method (Greenberg *et al* 1985).

3. Results and discussion

The difference between heterogeneous and homogeneous reaction mechanisms can be explained by comparing degradation of 4-CP and TOC (figures 1 & 2). Degradation curves of 4-CP and TOC in the UV/TiO₂ and UV/TiO₂/H₂O₂ experiments show a similar course, in contrast to homogeneous reactions, where the 4-CP concentration decreases more rapidly than TOC-concentration. During the dark Fenton reaction, 4-CP disappears rapidly within a few minutes but TOC removal is only 42% after 24 hours. With photolysis in the presence of a 10:1 excess of H₂O₂, 4-CP is completely degraded after 24 hours with a TOC reduction of only 51%. A very high excess of H₂O₂ reduces the degradation rates of both 4-CP and TOC because of recombination of the hydroxyl radicals (Carey 1990).

In case of UV/TiO₂, the pollutant has to be adsorbed before reaction. This explains the low degradation rate of 4-CP. In solution, there are more free substrate molecules and more OH-radicals for reaction, therefore 4-CP concentration in homogeneous processes decreases very rapidly. Hydroxyl radicals are able to attack the molecules without steric restrictions in contrast to the 4-CP molecule adsorbed on the

Figure 1. Degradation of 4-chlorophenol (1.01 mmol/l = 72.9 ppm TOC) with different homogeneous and heterogeneous methods.

Figure 2. Degradation of TOC (72.9 ppm = 1.01 mmol/l 4-CP) with different homogeneous and heterogeneous methods.

TiO₂-surface. In this case, a molecule has to be degraded nearly completely to CO₂ and to desorb before a new molecule can take its place. Therefore, the amount of by-products formed during the heterogeneous process is small compared to Fenton's reagent or UV/H₂O₂. Among the described wastewater treatment methods, the system UV/TiO₂/H₂O₂ combining homogeneous and heterogeneous reactions, was found to be the best degradation method for TOC. TOC degradation was about 80% after 24 hours.

In all processes degradation of H₂O₂ (figure 3) follows the curves of TOC degradation (figure 2). The most rapid decrease of H₂O₂ was observed with Fenton's reagent.

Figure 3. Decrease of H₂O₂ during reaction.

After one hour, the reaction retards because of complete oxidation of Fe²⁺ to Fe³⁺, (2). Fe³⁺ can be re-reduced during excitation with visible light ($\lambda < 580$ nm) (Ruppert and Bauer 1993). The presence of TiO₂ in the UV/H₂O₂ process accelerates the degradation of H₂O₂.

For industrial use, homogeneous processes like UV/H₂O₂ (Hager 1990) and UV/ozone (Kearney *et al* 1984) are preferred to heterogeneous processes because of higher degradation rates and no separation problems with the catalyst. In recent years, reactors with immobilized TiO₂ have been developed to avoid this problem (Al-Ekabi and Serpone 1988; Hofstadler 1992; Hofstadler *et al* 1992).

Indeed, photochemical oxidation is an effective way to destroy organic water pollutants although the process has to be optimized and adapted to the contaminant and its concentration.

Acknowledgements

The authors would like to thank the FFF (Forschungsförderungsfonds der Gewerblichen Wirtschaft Österreichs, P 3/8669) for their financial support.

References

- Al-Ekabi H and Serpone N 1988 *J. Phys. Chem.* **92** 5726
- Barbeni M, Minero C and Pelizzetti E 1987 *Chemosphere* **16** 2225
- Carey J H 1990 *Proc.-Symp. Adv. Oxid. Processes Treat. Contam. Water Air* (Burlington/Ontario: Wastewater Technol. Center) Paper No. 1
- Greenberg A E, Trussel R R and Clesceri L S (eds) 1985 *Standard methods for the examination of water and wastewater* (Washington: Am. Public Health Assoc.) p. 426
- Haag W R and Yao C C D 1992 *Environ. Sci. Technol.* **26** 1005
- Hager D G 1990 *Innovative Hazard. Wastes Treat. Technol. Ser.* **2** 143

- Hofstadler K 1992 *Development of a photocatalytic reactor with immobilized TiO₂ for wastewater purification*, Doctoral thesis, Technical University, Vienna
- Hofstadler K, Ruppert G, Bauer R, Heisler G and Novalic S 1993 In *Photocatalytic purification and treatment of water and air* (eds) D F Ollis and H Al-Ekabi (Amsterdam: Elsevier) pp. 777–782
- Kearney P C, Zeng Q and Ruth J M 1984 *ACS Symp. Ser.* **259** 195
- Matthews R W 1987 *Sol. Energy* **38** 405
- Moza P N, Fytianos K, Samanidou V and Korte F 1988 *Bull. Environ. Contam. Toxicol.* **41** 678
- Ruppert G and Bauer R 1993 *J. Photochem. Photobiol.* **A73** 75
- Yasuhara A, Otsuki A and Fuwa K 1977 *Chemosphere* **10** 659