Ph.D. Thesis

Applications of low-pressure mercury vapor lamps for decompositing organic pollutants in water and air

Tünde Alapi

University of Szeged
Ph.D. School of Environmental Sciences
Department of Inorganic and Analytical Chemistry

2007

1. Introduction and aims

The pre-treatment and treatment of air and waters continuously attract significant interest due to the presence of compounds in natural waters that are difficult to eliminate by conventional chemical and/or biological methods. The toxicity of the pollutants and the high costs associated with the available methods recently created a pressing need for the development of more efficient processes.

The advanced oxidation processes (AOPs) are emerging technologies, which have been developed for treatment of air and water containing hazardous pollutants. The potential of these methods to remove both organic and inorganic compounds is currently being intensively studied. The AOPs, among others, include direct ultraviolet (UV) and vacuum ultraviolet (VUV) photolysis. In addition to these, nowadays, heterogeneous photocatalysis can be seen as one of the most favored research topics due to its promising applicability both in water and air treatment and solar energy utilization. The continuously growing interest in the application of AOPs has triggered a wealth of publications in the literature nevertheless the direct comparison of their efficiency under identical experimental conditions is scarce. On the other hand, researchers generally investigate the decomposition of one target compound, but during the treatment of polluted air or (waste)waters the decomposition of several compounds should be achieved in parallel. In a system like this, the compounds can affect each others' decomposition.

An objective of the present Ph.D. thesis is the comparison of various AOP processes (UV photolysis, combined UV/VUV photolysis and heterogeneous photocatalysis) through the decomposition of phenol and its intermediates using the same experimental apparatus and low-pressure mercury vapour lamps having identical geometric and electric parameters. The UV/VUV decomposition of chlorinated methanes (as potential air pollutants) and their binary mixtures in the gas phase was also investigated to study a multicomponent system.

2. Experimental conditions and methods

2.1. UV/VUV photolysis of chlorinated methanes in the gas phase

The photolysis of the chlorinated compounds was investigated by using a low-pressure mercury vapour lamp emitting both at 254 (6.15×10^{-6} einstein s^{-1}) and 185 nm (3.55×10^{-7} einstein s^{-1}). This light source was centered in a tubular glass reactor. The thickness of the irradiated gas layer was 2 mm, thus, the reactor volume is considered to be irradiated homogeneously. The flow rate of high purity (99.995%) nitrogen or oxygen gas was 98 cm^3 min^{-1} and the residence time was estimated to be 17.5 s. The liquid VOCs (CH_2Cl_2, $CHCl_3$ and CCl_4) or their binary mixtures were injected into the gas stream by means of a syringe pump through a sample port sealed with a Teflon septum.

Under oxygen-free conditions the composition of outgoing gas stream was analyzed by gas chromatographs equipped with flame ionization detectors. Qualitative analysis was carried out by using GC/MS. For photodecompositions in oxygen stream, FTIR (Fourier Transform Infrared) spectroscopy was applied to measure the concentrations of chlorinated compounds, their products (CO, CO_2, $COCl_2$, HCl) and the O_3 formed. The maximum concentration of O_3 was 3.60×10^{-5} M.

2.2. UV, UV/VUV photolysis and heterogeneous photocatalysis of phenol in aqueous solutions

The decomposition of phenol by using different AOPs was investigated by using the same apparatus. The light source was centred in the water-cooled, double-walled glass tubular reactor. The light source was immersed directly into the solution/suspension, which was circulated continuously around the lamp. The solution was thermostated at 25±0.5 °C. Oxygen or nitrogen gas was bubbled through the aqueous solution/suspension during the experiments.

The light sources were low-pressure mercury vapour lamps having identical geometry and electric parameters (15 W). A low-pressure mercury vapor lamp covered with commercial quartz (UV lamp), emitting only at 254 nm (5.97×10^{-6} einstein s^{-1}) was used to study the UV photolysis of phenol ($\varepsilon_{254\ nm} = 516\ dm^3\ mol^{-1}\ s^{-1}$). In the UV/VUV decomposition of phenol a low-pressure mercury vapour lamp covered with high purity silica quartz (UV/VUV lamp) was applied, which emits both at 254 nm (5.97×10^{-6} einstein s^{-1}) and 185 nm (3.6×10^{-7} einstein s^{-1}). In the heterogeneous photocatalytic investigations a UV lamp or a special mercury vapour lamp (emits in the 300-400 nm region, 7.23×10^{-6} einstein s^{-1}) was used.

The degradation of phenol was characterized by a linear fit to the decay curve of phenol, above 20% conversion ($0.988<R^2 < 0.997$).

The concentration of phenol, aromatic intermediates (1,2- and 1,4-dihydroxybenzene) and organic acids were determined with an HPLC system, equipped with a Merck-Hitachi L-4250 UV-Vis detector. The concentration of the alkylhydroperoxide was measured by the enzyme catalysed transformation of leuco crystal violet. The total organic carbon concentrations (TOC) of the solutions investigated were measured by using a Euroglas 1200 TOC apparatus.

3. Results

3.1. UV/VUV photolysis of the chlorinated methanes and their binary mixtures under oxygen-free conditions

1. The rate of degradation of both HCl_3 and CH_2Cl_2 was found to be significantly higher than that of CCl_4. This is due to the relative contribution of the •Cl initiated H-abstraction reactions to the decomposition of the H-containing chlorinated methanes, which was confirmed by the products distribution. The apparent quantum yield of the decomposition of CCl_4 was less than unity, while that of CH_2Cl_2 and $CHCl_3$ exceeded unity.
3. Addition of CCl_4 to CH_2Cl_2 or $CHCl_3$ caused a significantly higher rate of decomposition of the H-containing chlorinated methanes, which was explained by the higher •Cl concentration. In the case of the photolysis of these binary mixtures the CCl_4 plays a role of a •Cl source. The effect of CCl_4 on the relative contribution of the •Cl initiated H-abstraction reactions to the decomposition of CH_2Cl_2 or $CHCl_3$ was proved by the product distribution. Addition of CH_2Cl_2 to $CHCl_3$ caused a significant decrease in the rate of degradation of the $CHCl_3$, because the CH_2Cl_2 plays a role of a •Cl scavenger. This was confirmed by the inhibitory effect of the CH_2Cl_2 on the formation of CCl_4 as product.

3.2. UV/VUV photolysis of the chlorinated methanes and their binary mixtures in an oxygen stream

1. In oxygen stream ozone formed due to the absorption of 185 nm light by oxygen. The efficiency of the combination of the ozone and 254 nm UV light is negligible comparing to that of the synergic effect of 185 and 254 nm light in the decomposition of the target substances.
2. The rate of degradation of CH_2Cl_2 and $CHCl_3$ increased dramatically with their initial concentrations, because the •Cl initiated chain reaction determines the decomposition of these substances above a given concentration. In oxygen stream, the further transformations of the peroxyl radicals and phosgene formed create new pathways for the formation of •Cl.
3. In humidified oxygen stream, the HO• formed opens up new pathway for the decomposition of $CHCl_3$ and CH_2Cl_2, consequently, their rate of degradation increased with the increasing concentration of water. At the same time, the concentration of HCl

decreased, because of the competition between the H-abstraction reactions initiated by HO• and •Cl.

4. In oxygen stream addition of $CHCl_3$ enhanced the decomposition of CH_2Cl_2 and addition of CH_2Cl_2 has no inhibitory effect of the degradation of $CHCl_3$ opposite to that observed in nitrogen stream. These observations are consistent with that, the further transformations of peroxyl radicals results in •Cl.

3.3. UV, UV/VUV photolysis and heterogeneous photocatalytic decomposition of phenol in aqueous solutions

1. In TiO_2 containing suspensions irradiated with 254 nm light, the UV photolysis of phenol had a minor role, because of the competitive light absorption between phenol and TiO_2. The reactions occurred in a very thin layer of the suspension.
2. In UV irradiated solutions, dissolved oxygen enhanced both the rate of degradation and the apparent quantum yield of phenol. Due to the absorption of 254 nm light, the photoionization of phenol undergoes, and results in phenoxyl radical accompanied with the formation of $HO_2^{\bullet}$ and/or $O_2^{\bullet-}$. Thus, in UV irradiated solutions oxygen has a role of an electron scavenger, while the formation of the reactive species (such as $HO_2^{\bullet}$, $O_2^{\bullet-}$ and peroxyl radicals) opens up new possibilities for the further transformation of phenol.
3. The rates of the decomposition of phenol in UV/VUV irradiated solutions exceeded the values obtained for UV irradiated ones. The VUV photons generate HO• and •H from water. Dissolved oxygen inhibits the recombination of these primary radicals, consequently, causes higher concentration of HO• and $HO_2^{\bullet}$ and enhanced rate of degradation of phenol.
4. Inhibitory effect of methanol as HO• scavenger was also investigated. Addition of methanol has no effect in UV irradiated solutions. In UV/VUV irradiated ones the degree of the inhibitory effect decreased strongly with initial concentration of phenol, proving that the relative contribution of the HO• based reactions to the decomposition of phenol decreased. The inhibitory effect of methanol was found to be much more significant in UV irradiated TiO_2 containing suspensions. Our results demonstrate that the transformation of phenol in these suspensions takes place mainly by HO• based reactions.
5. When a more effective radical scavenger (NaN_3) was applied the rate of decomposition strongly decreased both in UV and UV/VUV photolysis. At the same time, there was not

any difference between the degradation rates determined in UV and UV/VUV irradiated solutions. This observation proved the considerable contribution of the $HO_2^{\bullet}$ and/or $O_2^{\bullet -}$ to the photooxidation of phenol both in UV and UV/VUV irradiated solutions.

3.4. Formation and transformation of the aromatic intermediates

1. In oxygen-free solutions, the radicals formed rapidly recombine. Oxygen inhibits the recombination, and creates possibility for the formation of the 1,2- and 1,4-dihydroxybenzenes as aromatic intermediates. In all cases the formation and decomposition of these aromatic intermediates takes place together with the decomposition of phenol.
2. In UV irradiated solutions the concentration of 1,2-dihydroxybenzene exceeded that of 1,4-dihydroxybenzene in great measure. Their formation is due to the recombination of the phenoxy radical and $HO_2^{\bullet}$, and is followed by the H_2O elimination. Thus, the formation of 1,4-dihydroxybenzene is likely to be stericaly hindered.
3. In UV irradiated TiO_2 suspensions, the concentration of 1,4-dihydroxybenzene exceeded that of 1,2-dihydroxybenzene, however, 1,2-dihydroxybenzene is expected to be dominant. This observation could be explained by the fact that, the reactions take place on the surface of the TiO_2 particles under stericaly hindered conditions. The effect of the TiO_2 concentration on the product distribution confirmed this assumption.
4. In oxygen-free, UV irradiated solutions the rate of degradation of phenol and dihydroxybenzenes increased according to their molar absorptivity. In solutions saturated with oxygen, the rate of degradation of 1,4-dihydroxybenzene exceeded that of 1,2-dihydroxybenzene in spite of the fact that, its molar absorptivity is much lower. This observation confirmed the considerable contribution of the $HO_2^{\bullet}$ and/or $O_2^{\bullet -}$ to the photooxidation of these aromatic compounds. The rate of photooxidation of the aromatic compounds investigated in TiO_2 suspensions and in U/VUV irradiated solutions exceeded the values determined in UV irradiated ones, because their photooxidation is primarily determined by the $HO\bullet$.

3.5. Formation and transformation of the aliphatic intermediates

1. Besides aromatic intermediates, aliphatic carboxylic acids are also formed, proving the opening of the aromatic ring and fragmentations of intermediates in all cases.

2. Among the aliphatic intermediates detected, the photooxidation of maleic, tartaric and oxalic acid was investigated. UV photolysis was found to be ineffective in the oxidation of maleic and tartaric acid. The degradation of oxalic acid commenced with an induction period, whose duration decreased with increasing initial concentration. Applying UV/VUV photolysis or heterogeneous photocatalysis, the decomposition of aliphatic intermediates was found to be much faster.
3. In UV and UV/VUV irradiated solutions the accumulation of oxalic acid together with the decrease in the total organic carbon concentration became considerable after the total decomposition of phenol and dihydroxybenzenes. This suggests that the fragmentation of the longer-chain carboxylic acids becomes significant only after the disappearance of aromatic compounds. At the same time, in UV irradiated TiO_2 suspensions, the decrease of the total organic carbon concentration started together with the decomposition of phenol and the accumulation of the oxalic acid is not significant. Comparing these processes, the heterogeneous photocatalysis is the most efficient method in the total mineralization of phenol.

List of publications

Publications directly associated with the theses

Refereed publications

1. Alapi, T., Van Craeynest, K., Van Langenhoeve, H., Dombi, A.
   UV photolysis of the binary mixtures of VOCs in dry nitrogen stream
   React. Kinet. Catal. Lett. 87, 2006, 255-267 IF (2004): 0,618
2. Alapi, T., Van Craeynest, K., Van Langenhoeve, H., Dewulf, J., Dombi, A.
   Direct VUV photolysis of chlorinated methanes and their mixtures in nitrogen stream
   Chemosphere, 66, 2007, 139-144 IF(2005): 2,297
3. Alapi, T., Dombi, A.
   Direct VUV photolysis of chlorinated methanes and their mixtures in oxygen stream using an ozone producing lamp
   Chemosphere, 67, 2007, 693-701 IF(2005): 2,297
4. Alapi, T., Dombi, A.
   Comparative study of the UV and UV/VUV photolysis of phenol in aqueous solution
   J. Photocehem. Photobiol. A: Chemistry
   (in press:10.1016/j.photochem.2007.01.002) IF(2005): 2,286
   www.sciencedirect.com

Full conference papers

5. Alapi, T., Dombi, A., Van Craeynest, K., Van Langenhove, H.
   UV photolysis of binary mixtures of VOCs in nitrogen stream
   The 11th Symposium on Analytical and Environmental Problems
   Hungary, Szeged, 2004. 09. 27. pp.
   poster
6. Alapi, T., Dombi, A., Van Craeynest, K., Van Langenhove, H., Dewulf, J.
   UV photolysis of binary mixtures of VOCs in dry nitrogen stream
   Advanced Oxidation Processes as Abatement Technologies for Organic Micropollutants, Belgium, Ghent, 2004. 03. 12. (5/ p. 1-7.)
   oral presentation
7. Alapi, T., Dombi, A., Van Craeynest, K., Dewulf, J., Van Langenhove, H.
   Decomposition of chlorinated methanes by UV-light in gas stream
   17th International Ozone Assosiation World Congress
   France, Strasbourg, 2005. 08. 22-25., CD Ed.
   lecture

8. Alapi, T., Dombi, A.
   Comparative Study of the UV and UV/VUV Photolysis of Phenol in Aqueous Solution by Using Different Types of Low-pressure Mercury Lamps
   International Conference Ozone and UV Sustainable Solutions for Industry and the Environment
   Germany, Berlin, 2006. 03. 04., CD Ed.
   lecture

9. Alapi, T., Beretka, N., Dombi, A.
   Fenol vizes oldatának UV és UV/VUV fotolízise valamint heterogén fotokatalitikus bontása
   II. Kárpát-medencei Környezettudományi Konferencia
   Hungary, Pécs, 2006 06. 1-2., CD Ed.
   oral presentation

10. Ilisz, I., Alapi, T., Gajdáné, Schrantz K., Ambrus, Z., Balázs, N., Sipos, P., Dombi, A.
    Nagyhatékonyságú oxidációs eljárások a környezeti kémiában
    II. Kárpát-Medencei Környezettudományi Konferencia
    Hungary, Pécs, 2006 06. 1-2., CD Ed.
    lecture

11. Dombi, A., Alapi, T.
    Comparision of direct photolysis and heterogeneous photocatalysis of phenol in aqueous solution
    1st European Conference of Environmental Applications of AOPs
    Greece, Chaina, 2006. 09. 07-09., CD ed.
    poster

Conference abstracts associated with the theses

1. Alapi, T.
   Szerves gyökök reakciói metanol és fenol vizes oldatának vákuum-ultraibolya fotolízise során
   XXV. Kémiai Előadói Napok
   Hungary, Szeged, 2002. 10. 28-30.
   lecture

2. Alapi, T., Dombi, A., Van Craeynest, K., Van Langenhove, H.
   Decomposition of chlorinated methanes by UV-light in gas stream
   Perspectives of Photochemistry in the New Millenium
   Austria, Badgastein, 2004. 03. 7-11.
   poster

3. Alapi,T., Dombi, A.
   Effect of methanol as hydroxil radical scavenger on the VUV photolysis of phenol in aqueous solutions
   The 2nd European Conference on Oxidation and Reduction Technologies for Ex-situ and In-situ Treatment of Water, Air and Soil
   Germany, Gottingen, 2005. 06. 12-15.
   lecture

4. Alapi, T., Dombi, A., Van Craeynest, K., Van Langenhove, H., Dewulf, J.
   UV photolysis of bynary mixtures of chlorinated methanes in oxygen and nitrogen stream
   The 2nd European Conference on Oxidation and Reduction Technologies for Ex-situ and In-situ Treatment of Water, Air and Soil
   Germany, Gottingen, 2005. 06. 12-15.
   poster
5. Alapi, T., Dombi, A.
   Comparison of the direct photolysis and heterogeneous photocatalysis of phenol
   Solar Chemistry and Photocatalysis: Environmental Application
   Spain, Las Palmas, 2006. 11. 8-10. pp. 30.
   lecture
6. Alapi, T., Pallagi, A., Szabó, R., Dombi, A.
   Comparison of the UV-induced photolysis of phenol in water and acetonitrile
   ICP2007 –XIII. International Conference on Photochemistry
   Germany, Köln, 2007. 07. 29- 08. 03.
   poster, accepted for presentation
7. Alapi, T., Sipos, P., Berecz, L., Dombi, A.
   Comparison of the UV-induced photolysis, ozonation and their combination in the decomposition of phenol
   ICP2007 –XIII. International Conference on Photochemistry
   Germany, Köln, 2007. 07. 29- 08. 03.
   poster, accepted for presentation
8. Alapi, T., Dombi, A.
   Comparative study of the UV and UV/VUV-induced photolysis and heterogeneous photocatalysis of phenol focused on the intermediates
   International Ozone Association – International Ultraviolet Association Proceedings, 2007 IOA-IUVA Joint World Congress
   United States of America, California, Los Angeles, 2007. 08. 27-29.
   lecture, accepted for presentation
9. Alapi, T., Dombi, A.
   Comparison of the efficiency of UV-induced photolysis, ozonation and their combination in the decomposition of phenol
   International Ozone Association – International Ultraviolet Association Proceedings, 2007 IOA-IUVA Joint World Congress
   United States of America, California, Los Angeles, 2007. 08. 27-29.
   lecture, accepted for presentation

Publications not directly associated with the theses

Refereed publications

1. Alapi, T., Sipos, P., Ilisz, I., Wittmann, Gy., Ambrus, Z., Kiricsi, I., Mogyorósi, K., Dombi, A.
   Synthesis and characterization of titania photocatalysts: The influence of pretreatment on the activity
   Appl. Catal. A: General, 303, 2006, 1-8 IF(2005): 2,728

Full conference papers

2. Alapi, T., Ilisz, I., Dombi, A., Méhn, D., Kiricsi, I.
   Enviromental Decontamination and Solar Energy Utilization Using Heterogeneus Photocatalysis as a Promising Alternative
   Young People and Multidisciplinary Research, The IVth International Symposium
   Romain, Timisora, 2002. 11. 14-15. CD Ed.
   poster
3. Alapi, T., Ilisz, I., Dombi, A., Mogyorósi, K., Kiricsi, I.
   Block Copolymer Templating Synthesis of mesoporous Titania Photocatalyst
   The 4th International Conference on Carpatian Euroregion Ecology
   Hungary, Miskolc-Tapolca, 2003. 04. 28-30. CD Ed
   poster
4. Alapi, T., Sipos, P., Ilisz, I., Dombi, A., Kiricsi, I., Mogyorósi, K.
   Synthesis and characterization of mesoporous titania photocatalysts
   Advanced Oxidation Processes as Abatement Technologies for Organic Micropollutants.
   Belgium, Ghent, 2004. 03. 12. (7/p. 1-9.)
   lecture
5. Alapi, T., Sipos, P., Ilisz, I., Wittmann, Gy., Dombi, A., Kiricsi, I.
   Synthesis and characterizatiopn of mesoporous titania photocatalysts. Application of ozone for the removal of the structure forming template
   17th International Ozone Assosiation World Congress
   France, Strasbourg, 2005. 08. 22-25. Cd Ed
   poster

Conference abstracts not directly associated with the thesis

1. Alapi, T., Dombi, A.
   Synthesis and characterizatiopn of mesoporous titania photocatalysts the influence of pretreatment on the activity
   Solar Chemistry and Photocatalysis: Environmental Application
   Spain, Las Palmas, 2006. 11. 8-10 pp. 232.
   poster
2. Wittmann, Gy., Alapi, T., Dombi, A.
   Synthesis and characterization of mesoporous titania-silica photocatalysts
   Perspectives of Photochemistry in the New Millenium
   Austria, Badgastein, 2004. 03. 07-11.
   poster